# RUBBER CHEMISTRY AND TECHNOLOGY

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## RUBBER CHEMISTRY AND TECHNOLOGY

# THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

UNITED STATES CIVIL SERVICE COMMISSION
WASHINGTON, D. C.

## CROP–PRODUCTION SPECIALISTS IN RUBBER, OIL–PRODUCING, AND TROPICAL PLANTS NEEDED

Persons with a practical knowledge of the production of rubber and oil-producing crops and other tropical plants, including the procurement of wild rubber, are being sought for Federal employment, the Civil Service Commission announced on February 8, 1943.

The positions range from chief crop-production specialist, at $8,000 a year, to the assistant grade at $2,600 per year.  Overtime on the basis of a standard work-week of 48 hours (which includes 8 hours overtime) is paid on salaries up to $5,000 per year.  While some positions will be filled in the United States, a majority of them will be filled outside its continental limits, principally in the South and Central American countries.  Additional compensation will be paid to persons appointed for duty outside the United States, to be determined by the loaction of the position.  Applicants who have a speaking knowledge of Spanish, Portuguese, or French should include this information in their application forms.

Persons appointed will do work in connection with the establishment and operation of research stations or plantations growing rubber or oil-producing plants.  Plantations will be situated, for the most part, in remote and primitive areas.  The duties will involve making surveys of the country to determine the selection of proper sites, soils, and other essential factors.

There are three options: rubber plants, oil-producing plants, and other tropical plants, and experience in any of the three is acceptable.  Applicants must have had sufficient experience to insure a practical knowledge of the production of any one of them, which may have been acquired in their growing, or in research, extension, or closely allied work.  In general, at least 6 months of such experience must be shown for the assistant grade, at $2,600.  The minimum requirements for the higher grades are proportionately higher.  For some positions, persons are desired who have had education with major study in agronomy, horticulture, plant breeding, forestry, or other courses related to plant production, in addition to the required experience.

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Applications will be accepted until the needs of the service have been met, but qualified persons are urged to apply immediately.   There are no age limits, and no written examination will be given.   Applications and complete information may be obtained at first- and second-class post offices, from civil service regional offices, and from the U. S. Civil Service Commission, Washington, D. C.

Applications are not desired from persons already using their highest skills in war work.   War Manpower restrictions on Federal appointments are given in Form 3989, posted in first- and second-class post offices.

## NEW BOOKS AND OTHER PUBLICATIONS

PLASTICS CATALOG—1943.   Published by the Plastics Catalogue Corp., 122 E. 42nd St., New York, N. Y.   Cloth 9 x 12 inches.   864 pages.   $5.— This year's edition of the "Plastics Catalog", the largest ever published, is indeed worthy of the supplementary classification as "An Encyclopedia of the Plastics Industries".   The first section, "Plastics at War", gives details and illustrations of the applications of plastics in every arm, branch, and bureau of the government where plastics have been used.   A list of government offices maintaining procurement contacts with plastics manufacturers is included.   A section on synthetic rubbers, entitled, however, "Rubberlike Plastics", contains interesting articles on all the various synthetic rubbers, and includes a chart on the properties of synthetic rubbers, based on data furnished by the private manufacturers of these rubbers.   The catalog contains ten sections, in all, in addition to an article on the history of plastics.   The section on materials covers every type of plastic moulding material, filler, coloring material, plasticizer, and solvent now being commercially used.   This section contains three extensive charts of special interest: (1) plastics properties chart, (2) plasticizer properties chart, and (3) solvents properties chart.   Another chart, new in this edition, is on chemical formula of plastics, resins and synthetic rubbers.   The section on manufacture gives flow sheets of basic materials and manufacturing processes.   The section on moulding and fabricating is very comprehensive, and includes about 30 articles on these subjects.   Other sections cover moulding and fabricating, machinery and equipment, laminates, plywood and vulcanized fiber, coatings, synthetic fibers, etc.   The directory section of the new catalog contains a detailed analysis of the available equipment in plastics manufacturers' plants.   A bibliography and glossary, an index of moulders' marks, and a complete index of manufacturers are further important features.   [From the *India Rubber World*.]

SCIENCE IN PROGRESS.   (Third Series.)   Edited by George A. Baitsell. Published by the Yale University Press, New Haven, Conn. 6 x 9¼ in.   322 pp. 112 ill.   $3.00.—Three years ago it was decided to issue a series of annual publications based on the National Sigma Xi Lectures.   Each annual volume contains important contributions from ten leaders in various scientific fields. This book is the third in the annual series published to date.   In addition to contributions from authorities in the fields of astronomy, biology, physics, and medicine, it contains a chapter on "Some Scientific Aspects of the Synthetic Rubber Problem", by Hermann Mark, of the Polytechnic Institute of Brooklyn. Professor Mark describes the molecular structure of high polymers, including polyethylene, polyvinyl alcohol, polyvinyl chloride, polyisobutylene, and polyvinyl acetate, and then discusses the association between some properties of these polymers and their structures.   He uses the following as the main criteria for describing the structure of the polymers: (1) the average molecular weight

or chain length; (2) the chain-length distribution curves; (3) the amount of branching or cross-linking; and (4) the magnitude and geometrical distribution of the intermolecular forces. The influence of each of these factors on the mechanical behavior of the respective materials is discussed. [From *The Rubber Age* of New York.]

The House of Goodyear (2d Edition.) By Hugh Allen. Published by Goodyear Tire & Rubber Co., Akron, Ohio. 6 by 9 in. 417 pp. $2.00.— Although, like the first edition, this book is the story of the birth and growth of the tremendous Goodyear organization, it is also the story, very well told, of rubber which, as the genial Mr. Allen puts it, has been "taken from the laboratory (by the fall of Malaya and the Netherlands Indies) and put on the front page of the nation's newspapers". As Mr. Allen so ably says, rubber is no longer an academic question. Therefore, although the book is written primarily for the internal industry audience, it contains phases of much wider interest. The current edition brings up-to-date the ever-fascinating tale of rubber its earliest history to its growth as a billion-dollar industry transferred bodily from one hemisphere to another and now starting back, from the smuggling of seeds out of Brazil by Wickham in 1876 by tramp steamer, to the delivery of seedlings by Clipper planes in 1941. The many international struggles for the control of rubber are exceptionally well handled and clearly portrayed for the noninitiate. The effects of rubber on such diverse personalities as William Jennings Bryan, William Howard Taft and Winston Churchill are discussed. An authoritative section on synthetic rubber, indicative of the "dam-the-torpedo" attitude of American industry, is included. The prominent part played by various Goodyear technicians in the development of the growing synthetic rubber industry is interwoven in the telling. The book is divided into eight chapters, as follows: (1) Economic Heresis and Modern Business; (2) A History of the Company; (3) Materials: Rubber and Cotton; (4) Products: Tires; (5) Expansion: In United States; (6) Industrial Relations; (7) Distribution; (8) Defense Demands on Industry. Each chapter is split into numerous sections for the convenience of the reader. In addition, a Chronology of Rubber, from 1498 to 1942, a list of National Balloon Race Winners, a list of International Races, and a complete subject index are included. [From *The Rubber Age* of New York.]

Rubber: List of Publications. Letter Circular LC-707. United States Department of Commerce, National Bureau of Standards, Washington, D. C. 17 pages.—This bulletin gives a list of the publications, by members of the staff of the National Bureau of Standards, on the properties, uses, and products of rubber, and includes a table of contents for finding publications on various subjects in the bulletin. Included also is information on specifications for rubber products, both industrial and Federal. [From the *India Rubber World.*]

Service Notes on Buna-Carbon Compounding. Binney & Smith Co., 41 East 42nd St., New York, N. Y. 8½ by 11 in. 7 pp.—An outline of carbons available for the compounding of GR-S (Buna-S), including a brief description of practical considerations in connection with the processing and compounding of carbon-reinforced Buna-S stocks, is presented in this technical bulletin. Data are given covering the combustion-furnace, full-reinforcing, and channel-impingement blacks, with suggestions for nomenclature included. Data also prove that, whereas with natural rubber, addition of pigment progressively reduces elongation, carbon is necessary in the case of Buna-S to develop elongation. [From *The Rubber Age* of New York.]

THE CARBON REINFORCEMENT OF BUNA-S (GR-S.) Columbian Carbon Co. (Binney & Smith Co., Distributors), 41 East 42nd St., New York, N. Y. 5½ by 7¾ in. 152 pp.—This booklet, issued as Volume IV in the series published under the title of "Columbian Colloidal Carbons", examines the carbon reinforcement of Buna-S (GR-S) from a dual approach. First, the properties are related to the surface-area of the respective carbons as determined by the electron microscope and, secondly, by cross-graphing. In the first approach, the study reveals that Buna-S is entirely dependent on colloidal carbon for strength, tensile being improved 600 per cent. The evidence also indicates that carbon reinforcement is itself a component in Buna-S vulcanization and in this connection a new method is offered for recognizing carbon "starvation" in Buna-S. The cross-graphing approach serves to bring out the important differences in rate of change of properties with carbon surface and loading between different carbons. The study, in this connection, proves that tensiles are affected chiefly by surface-area, hardness by loading, rebound by both surface-area and loading, while carbon network structure makes its own distinctive contribution. The booklet also describes two new physical tests, termed "Shore Creep" and "Flex Crack Growth", respectively. The first is a new application of a universally known test, while the second embraces the use of a new measuring machine. [From *The Rubber Age* of New York.]

DU PONT RUBBER CHEMICALS. (Report No. 43-1.) Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware. 6¼ by 9¼ in. 144 pp.—The last edition of the report containing complete descriptions of all du Pont rubber chemicals, Neoprene and Neoprene latices was published in 1937. Its revision has been complicated by the rapidly dwindling supply of natural rubber and the growing availability of the newer synthetic rubbers. Because of the urgency of the situation, revisions of some parts of the original report have already been issued by du Pont in the form of individual technical reports. The titles of these special reports included: The Neoprenes, The Compounding of Buna-S, and Rubber Latex Compounding. The present publication is a revision of another portion of the 1937 report. It is divided into three parts, the first devoted to brief descriptions of all du Pont rubber chemicals, the second containing descriptions of du Pont rubber colors, and the third showing the solubilities of many of the chemicals in rubber, Neoprene and some common solvents. The compounding characteristics of the chemicals refer, in most cases, to behavior in rubber. Where the information is available, however, the amounts that should be used and the principal effects of the company's chemicals in Neoprene and in Buna-S stocks are given. [From *The Rubber Age* of New York.]

KOROSEAL HANDBOOK OF TECHNICAL INFORMATION. The B. F. Goodrich Co., Akron, O. Section I—General. 24 pages.—This publication is indicated as the first of a series to be issued as a technical service to keep the industry informed as to the physical, chemical, electrical and processing characteristics of Koroseal compounds, and to aid in their use. Section II is to cover Koroseal insulating and jacketing materials for the wire and cable industry; Section III will describe in detail the tests used to evaluate thermoplastic and thermosetting materials, and later sections will cover additional subjects of major importance. This first section is comprehensive in its coverage of the chemistry and physical properties of this plasticized polymerized polyvinyl chloride resin, and includes a table of physical constants, in which some of the properties, as tearing strength, flexibility, impact strength, and abrasion resistance, are compared qualitatively with natural rubber compounds. This discussion on plasticizers shows by means of charts how the physical and electrical properties of the

polymer may be varied by the addition of these materials. The compounding of Koroseal with materials ranging from wood flour through carbon blacks to silica and mica is also illustrated by means of charts. Mention is made of the addition of certain thermosetting polymers to Koroseal to produce finished products capable of being vulcanized. It is indicated that additional data on this type of material will be furnished in subsequent sections to be published later. Some uses of Koroseal, as in protective coatings, in many electrical applications, and for many types of mechanical goods items including moulded articles, are described. The details of the mixing of Koroseal compounds, both on the open mill and in the Banbury, are covered, as are other processing methods such as extrusion, calendering, and moulding, in a description of the manufacturing of finished products from this material. Brief mention is made of Koroseal solutions and gels in concluding this first section of the handbook. [From the *India Rubber World*.]

STORAGE AND HANDLING OF BUTADIENE, ISOBUTYLENE, STYRENE, AND ACRYLONITRILE. By James B. Garner, Ludwig Adams and Robert M. Stuchell. Mellon Institute of Industrial Research, Pittsburgh, Penna. 9 x 12 in. 12 pp.—Reprinted from the October, 1942, issue of *Petroleum Refiner*, this pamphlet represents the results of a comprehensive study of the storage and handling of butadiene, isobutylene, styrene and acrylonitrile, the four most common chemical substances used in relatively large quantities in the production of synthetic rubber. The study consisted of a search of the available literature, the compilation of data from several coöperating organizations to establish the physical and chemical characteristics of the four substances, and experimental work to determine the corrosive effect of the stored substances on steel containers, and the effect of the steel containers on the stored substances. The study was made by the Chemical Storage Fellowship maintained at Mellon Institute by the Pittsburgh-Des Moines Steel Co. [From *The Rubber Age* of New York.]

SOME PHYSICAL PROPERTIES OF BUTADIENE AND STYRENE. (Letter Circular LC-710). By Lawrence A. Wood and Catherine F. Higgins. National Bureau of Standards, Washington, D. C. 8 x 10½ in. 8 pp.—Based on both a search of the literature and the measurement of certain properties at the National Bureau of Standards, the values of butadiene and styrene, the materials copolymerized to make Buna-S, which are regarded by the Bureau as most reliable at the present time, have been collected and put into tabular form in this letter circular. They are currently presented to meet an immediate demand for such data, but the point is stressed that in most cases the data have not been checked by independent observations. Revisions will be made as further information becomes available. [From *The Rubber Age* of New York.]

PATENTS AT WORK. Office of the Alien Property Custodian, Washington, D. C. 8 x 10½ in. 25 pp.—Through the Office of the Alien Property Custodian, the United States Government now holds about 50,000 patents formerly owned by residents of enemy and enemy-occupied countries. These patents are offered for use by American industry. This pamphlet has been prepared to provide industry with a brief outline of the policies which have been adopted for the administration of these patent holdings. There is also included an index to the classified lists of vested patents for use as a guide in ordering specific sections. [From *The Rubber Age* of New York.]

UNLOADING INFLAMMABLE LIQUIDS. Manual Sheet TC-4. Manufacturing Chemists' Association of the United States, 608 Woodward Bldg., Washington,

D. C.   12 pages.—This manual sets forth detailed directions for use in unloading tank cars of inflammable products which are liquid under ordinary atmospheric conditions, and should be useful for that portion of the rubber industry now involved in the manufacture of synthetic rubber in which such operations may be required.   Included in the manual are directions for tank-car handling when received at the plant, safety rules, details of tank-car dome fittings, and instructions for sampling.   Various unloading methods are described.   Piping to storage tanks, pumphouse equipment, and handling of empty cars for the return to supplier are also included.   Figures are given to illustrate proper unloading procedure.   [From the *India Rubber World*.]

CHEMICAL TECHNICAL DICTIONARY (GERMAN-ENGLISH-FRENCH-RUSSIAN). By A. W. Mayer.   Published by Chemical Publishing Co., Inc., 234 King St., Brooklyn, N. Y.   5½ x 8½ in.   872 pp.   $8.00.—This dictionary, one of the most comprehensive grouping English, German, French and Russian, insofar as technical dictionaries are concerned, will prove very useful for those who wish to study the German, French and Russian technical literature.   As many a research worker has discovered, ordinary dictionaries very often fall short of satisfactory translations and definitions where technical terms are concerned. This is especially true of the Russian literature and, accordingly, technical dictionaries of this type are extremely helpful.   The dictionary is also recommended to translators of the four languages and to college students.   The translation of the dictionary was under the direction of Prof. B. N. Menshutkin and Prof. M. A. Bloch.   [From *The Rubber Age* of New York.]

ROGERS' MANUAL OF INDUSTRIAL CHEMISTRY.   (6th Edition.)   Edited by C. C. Furnas.   Published by D. Van Nostrand Co., 250 Fourth Ave., New York, N. Y.   6 x 9 in.   1685 pp.   501 ill.   2 vols.   $17.00.—The essential facts, figures, methods and operations of practically every important chemical industry in America, compiled and contributed by experts in each field, are contained in this latest, revised, up-to-date edition.   Fundamental knowledge needed in present-day chemical work, including economic factors, physical unit-operations, and chemical unit-processes, is furnished in the early chapters, and is then applied specifically to each industry, including the rubber industry.   This sixth edition is divided into 8 sections, with 45 chapters in all.   The sections are: Background of the Chemical Industry; Heavy Chemicals and Allied Products; Fuels and Their By-Products; Refractories and Allied Materials; Metallurgical Products; Surface Coatings; Products of Organic Synthesis; and Natural Organic Materials.   The subject of synthetic plastics is treated in the section on Products of Organic Synthesis, while that of rubber and rubberlike materials is handled in Natural Organic Materials.   The chapter on rubber was contributed by James W. Schade, former Director of Research, and Victor E. Wellman, Manager of the General Chemical Laboratories, of the B. F. Goodrich Co.   Dr. Schade retired from the company several months ago.   Although written in condensed form, the subject is thoroughly covered from plantation industry to finished product.   The authors treat with materials of the industry, processing methods, rubber products, and the chemistry of synthetic rubber. A recommended reading list for further study is given at the end of the chapter. Similar lists appear at the end of most of the chapters in the work.   This manual is, of course, one of the most complete encyclopedic reference works available on industrial chemistry, and merits a place on the library shelf of every laboratory.   Like its predecessors, this latest edition is printed in clear, legible style and has a completely cross-referenced index.   [From *The Rubber Age* of New York.]

# GROWING RUBBER IN NORTH AMERICA *

## H. L. Trumbull

The B. F. Goodrich Company, Akron, Ohio

Ever since war was forced upon us, with the subsequent capture by the Japanese of the Malay Peninsula and the Dutch East Indies, Americans have been groping for new sources of natural rubber to replace those cut off by our enemies. With startling dispatch, lands which produced 90 per cent of the crude rubber used by this country had been captured, and the supplies from another 7 per cent of the world's producing areas had been endangered by action against lines of communication with these sources.

The problem was not entirely new, because many farseeing people, both in government service and private business, had been concerned about our dependence on distant sources for what had become one of our essential materials in peace and war. They had made studies of domestic plants which might produce rubber in quantities sufficient for our necessities. The urgency of the task, however, was not so great then as it is now.

Early this year I was assigned by the Goodrich company to give this problem primary attention, and to call on any other resources of the organization for assistance whenever necessary. The purpose was to seek information and propose action which would benefit the nation, suffering under an acute shortage of natural rubber. The principal early parts of this work were the study and evaluation of all domestic plants known to produce rubber, and the discovery, if possible, of new sources of this vital material on our continent.

Of course, I was not alone in this research project, which is far too broad for either individuals or privately-financed laboratories to tackle single-handed. Distinguished authorities in the federal Bureau of Plant Industry, Bureau of Agricultural Chemistry and Engineering, the Forest Service, in other rubber companies, and in several universities have devoted themselves to this subject. Among the latter is Cornell University, where a coöperative research study was established under Lewis Knudson.

It is too early to correlate the results so far obtained by these groups. Actually, most of these projects are just getting well underway; therefore, I can relate, in the main, only the material uncovered by searches into the literature and unpublished records, consultations with government bureaus, interviews with scientific investigators, counsel with colleagues in the rubber and allied industries, trips into the field where plants are growing, and the collection and study of rubber produced from them. This report is submitted, not as the statement of a mission accomplished, but in the hope that it may serve as a guidepost for things to come.

At Cornell, Knudson and a number of his research colleagues are conducting studies which cover a wide field. Greenhouse and experimental field plantings, as well as collections of wild plant material, provide an extensive basis for their experiments, which promise to have an important bearing on our common problem. W. C. Geer of Ithaca has volunteered the facilities of his well-equipped rubber laboratory to assist the Cornell project.

In March and early April, an extended field trip was made to visit the project for growing guayule and selected field plantings, including those of *Cryptostegia grandiflora*. Visits were made to Stanford University, the Universities of California and Arizona, and California Institute of Technology to meet scientists who had studied plants that might offer interesting possibilities. Independent scientists of note, and a few individuals who had private collections of plants or were experimenting on greenhouse material, were also interviewed.

The author is indebted to scores of individuals who have willingly supplied valuable information and plant specimens, and to the help afforded by his colleagues, Edwin Newton and W. D. Stewart, formerly of this company's Tropical Research Laboratories at Kuala Lumpur, Federated Malay States.

One of the year's significant achievements was that of the late Henry G. Knight, head of the federal Bureau of Agricultural Chemistry and Engineering, for the prompt organization of projects to estimate the rubber content of plant materials by dependable methods and to conduct pilot-plant studies for the extraction of natural rubber. The latter are being conducted at both the Southern and the Eastern Regional Research Laboratories of the U. S. Department of Agriculture.

Among recent contributions to the study of "useful rubber" from domestic plants, that of McGavack[1] of the United States Rubber Company is outstanding.

Responsibility for obtaining increased amounts of wild rubber from the sister republics of this hemisphere is shared by the State Department, the Inter-American Relations Council, the Board of Economic Warfare, and selected representatives of the U. S. Department of Agriculture who were prepared to serve as technical experts in this field.

Fortunately the results of the extensive Edison-Ford survey, begun in 1927 and representing about 17,000 collections and analyses of specimens, have not been lost or neglected; Edison's records and plant collections were inherited by the scientists in the Bureau of Plant Industry. L. G. Polhamus reports that the study has been continued on the more promising plants. Two varieties of goldenrod, *Solidago leavenworthii* and *S. edisonsiensis*, selected by the bureau for study and improvement, give promise as yielders of rubber. In the improved strains the leaves, which store most of the rubber, show an average rubber content of 5–6 per cent, nearly double that of the earlier strains. The presence of impurities such as saponin complicates the problem of rubber recovery. These plants grow in the coastal region from Charleston, S. C., to southern Florida, and are propagated from stolons, with a fiftyfold annual increase. However, the plants grown from seed yield almost as well as the parents. Estimated yields of rubber per acre are 60–90 pounds the first year, and twice as much the second year. No difficulties are anticipated in the cultivation and harvesting of goldenrod.

The early attempts to derive rubber from goldenrod, based on solvent extraction processes, gave a product of inferior properties; it was sticky and puttylike, and in vulcanized form had only moderate tensile strength.

McGavack recently announced that, by digesting the 6 per cent rubber-bearing leaves with either acid or alkali for short periods at room or elevated temperatures, the rubber content can be increased to 30 per cent or higher. The resulting material is then subjected to pebble-mill treatment to effect flotation of the rubber; it is thus recovered relatively free from contaminants and in better condition than is possible by solvent extraction.

This observation is important in relation to the work actively in progress at the Southern Regional Research Laboratory, where more than a score of investigators are elaborating the methods of recovery of rubber from this plant. From the correlation of these studies, a rubber of better quality should result than that obtained in the solvent-extraction processes previously employed.

The Bureau of Plant Industry has also made studies of three varieties of *Cryptostegia*—namely, *C. grandiflora*, *C. madagascariensis*, and a hybrid described by Polhamus, Hill, and Elder[2]—a family yielding rubbers of excellent quality.

In their study of rubber from natural sources, the Russians are reported to have examined 100,000 plants in one year. The choice centered on one of three dandelions, *kok-sagyz*, a native of the mountainous region bordering China. In this plant, the vigorous root carries most of the rubber. A perennial, it is reported to give the best yields of rubber if harvested after its first year. Although a second season's growth favors larger roots, the loss of plants due to wintering more than offsets the growth factor. The roots, weighing about 30 grams each, are harvested as in beet culture. Yields of 30–60 pounds of crude rubber per acre are indicated by Brandes[3], although in published articles some of the Russian claims are more generous.

The Bureau of Plant Industry arranged to have seeds of *kok-sagyz* flown from Moscow this year by transport plane[3]. These seeds were planted in sixty different locations, mainly in the northern tier of states, check plantings being conducted in many instances with vernalized seed. The introduction of the Russian dandelion is an experiment which merits extensive study, since an abundant annual crop of latex-bearing roots would aid us fairly promptly. Data need to be garnered on the propagation, cultivation, and processing of this plant. The yields and properties of *kok-sagyz* rubber should be studied critically.

## GUAYULE

The publications of Lloyd[4], McCallum[5], Spence[6], Carnahan[7], and others have given us fuller knowledge of this desert wildling than of other domestic plants which yield rubber. Commercially this shrub is the sole source of rubber grown in the United States, but Mexico has supplied much larger amounts than have been produced here.

According to the records of the U. S. Department of Commerce, exports of guayule rubber from Mexico to the United States over a period of years have been as follows:

| Year | Raw rubber (long tons) | Year | Raw rubber (long tons) |
|---|---|---|---|
| 1905 | 335 | 1935 | 459 |
| 1910 | 9,842 | 1936 | 1,228 |
| 1915 | 1,386 | 1937 | 2,691 |
| 1920 | 982 | 1938 | 2,485 |
| 1925 | 3,781 | 1939 | 1,964 |
| 1930 | 1,095 | | |

The Intercontinental Rubber Company in 1912 initiated studies under W. B. McCallum which were to lead to plantations of guayule. After ten years of research, during which 4,000,000 plants were studied, McCallum selected three specimens which proved worthy of propagation. These strains excelled the wild shrub both in rubber content and in the lower resin content of the rubber. Consistent research by McCallum on the treatment of seed to

ensure viability, the methods of seedbed and field culture, the cycles of irriga-
tion and desiccation, together with his early studies on selection, comprise
thirty years of continuous application to one objective.   Spence and others
collaborated on the problems of processing the shrub and perfecting a uniform
commercial product.   Intercontinental Rubber Company located extensive
plantations near Salinas, California, from which large tonnages of rubber were
produced.

After a year in the seedbeds and four years in the field, the mature plants
(7000 per acre), weighing about 2 pounds each, carry up to 20 per cent rubber
by weight.

The shrub is uprooted, cut to short lengths, loaded into trucks, and stored
in the warehouse to mature the plant material, which improves the yield of
rubber in the disintegration and flotation processes which follow.   The process
consists of separating the rubber which floats (worms) from the woody tissues
heavier than water.   To enhance this separation, the worms are subjected to
pressure under water, thus collapsing air cells in the entrained bark and effect-
ing further sedimentation of the wood.   After drying in vacuum pans, the
rubber gives an acetone extract of about 18 per cent.

By modern compounding practice, the use of guayule containing as high
as 25 per cent resin can be tolerated with other grades of rubber, reclaim, or
synthetic rubbers, respectively.

Under the act of March 5, 1942, Congress authorized the U. S. Department
of Agriculture to take over the project of the Intercontinental Rubber Com-
pany at Salinas, involving the propagation, cultivation, harvesting, and proc-
essing of guayule rubber.   In March the Forest Service placed in charge of
the project the competent administrator, Major E. W. Kelley, and retained
the services of the research botanist, W. B. McCallum.

The metabolism of guayule shrub requires desiccation over most of the
growing season to favor the production of rubber.   Spence advocates close
planting to rob the soil of its moisture; this simulates desert conditions at an
earlier stage of the plant's growth.   On the basis of his experiments, Spence[8]
recommended that guayule be harvested after the first year instead of the one
year in the nursey and four years in the field as practiced by Intercontinental
Rubber Company.   The observations of Spence indicate that even higher
yields of rubber per acre might be made possible, compatible with the earlier
harvest.   The Forest Service has arranged a series of test plantings to deter-
mine the best methods of cultivation and harvest of this important crop.   It is
gratifying to report that the quantity of seed collected in 1942 will aggregate
about five times that of the earlier estimates.   In the program of the Forest
Service this year, scores of locations are being studied to determine their
suitability from the standpoint of soil and climatic conditions.   The seed
which is now available is adequate to plant more than the 75,000 acres author-
ized by Congress under the act of March 5.

Unlike succulent plants which respond to photosynthesis by storing rubber
as liquid latex, the guayule shrub has been shown by Lloyd[9] to enmesh the
rubber globule in minute cells (parenchyma), not in a system of connecting
tubes such as characterizes the plants from which latex can be tapped.

Morphologically, about four-fifths of the rubber in the mature shrub is in
the cortex, with a smaller amount within the medullary rays.   Since it is the
woody portion of the plant[5] which carries resin-forming cells, conceivably the
process of comminution and flotation on water which is employed commercially
contributes to the contamination of the product.   As evidence of that possi-

bility are cited contributions by Spence[10] on the aqueous dispersion of guayule from the shrub and an experiment[11] conducted in the laboratory of W. Stacom at Long Island City, N. Y. Guayule shrub shipped from Salinas was placed in water overnight, with a resulting weight increase of 25 per cent. These stalks were passed once through the Stacom horn angle machine at Long Island City; the expressed juices were largely a dispersion of rubber, *i.e.*, latex comprising 55 per cent of the rubber present in the shrub. By simple boiling, coagulation of the latex ensued. The firm dry sheet of resulting rubber gave an acetone extract of 13 per cent, a value lower than the customary 18–25 per cent shown by commercial samples of guayule. Sheets of guayule made by Spence by coagulating the latex from fresh plants showed corresponding acetone extracts of 5–8 per cent. Improvements in the processing of the guayule shrub which might give rubber of higher quality as well as higher yields are in progress.

## RABBIT BRUSH

The rabbit brush (chrysothamnus), a desert dweller like guayule, is distributed over ten western states. It grows well at elevations around 7000 feet, frequently on inaccessible rocky hillsides, and rarely occurs in solid stands. Authentic analyses of the rubber content, together with current estimates of the existing stands of rabbit brush, indicate that not more than 30,000 tons of rubber could result from the slaughter of this shrub. The estimates of Hall and Goodspeed[12], 150,000 tons, were too optimistic. Plant scientists have not favored the domestication of this slow-growing desert shrub.

Excellent studies of the rabbit brush as a source of rubber are being conducted in the Eastern Regional Research Laboratory. This work is typical of the contributions which government scientists are making and are destined to make in this time of need. The distribution of rubber in the plant (based on analyses) furnishes the key to unlock the parsimonious store of this precious material. In rabbit brush, as in guayule, the rubber occurs mainly in the cortex, and mechanical processing methods are probably indicated. The inevitable perfection of a process designed to handle woody material of 1 per cent rubber content would doubtless even enhance the yield of rubber from the guayule shrub, which carries from 7 to 20 per cent rubber.

## PLANTATION RUBBER

The history of plantation rubber development reveals an unfortunate record in the Americas concerning the latex yielders, mainly *Hevea* and castilla. Fundamentally the two basic causes for the failure of *Hevea* plantations were unfavorable economic factors and the attacks of a fungus, the South American leaf disease. In the case of castilla, the low yield of rubber rather than the leaf disease proved unfavorable. Disregarding economic factors, the high-yielding species *Hevea braziliensis* can, of course, be grown in the Americas since it is a native of the Amazon, but the selection of varieties not subject to blight is necessary to ensure survival of the planted trees. The work of Rands[13] and other scientists in the U. S. Bureau of Plant Industry has made American plantations[14] possible. At a number of tropical stations the bureau maintains plant material resistant to the South American leaf disease as well as high-yielding bud stock, and effects exchanges with interested planters. So limited are the operations of the latter, however, that no large quantities of rubber can be expected to come from American plantations during the

(Top) Wild plant of *Cryptostegia grandiflora* at least six years old.   (Below) Buds, blossoms, and nearly ripe seed pods of Cryptostegia all on the same plant.

emergency. Nearly ten years are required to bring nursery stock to the tapping stage.

That the bulk of the world's rubber has come from the *Hevea* tree is more than accidental. Of the tropical sources, *Hevea* rubber had the best properties, the trees were the steadiest yielders, responded to tappings repeated indefinitely, and the yields were high. These considerations should aid us in pointing the way to a domestic crop which may be made to serve as a source of rubber. Ideally, we should look for a source in the form of an annual crop which will supply abundant high-quality yields per acre every year, in the form of either latex or rubber. Many of our manufacturing operations require latex. Emphasis should be placed on quality, since so much of our rubber has been based on the high-quality *Hevea* grades.



*Courtesy, The News, New York's Picture Newspaper.*

Experimental collection of *Cryptostegia* latex.

Examination of the literature affords surprisingly little accurate information on which to base the choice of crop materials suitable for the growth of rubber. Most of the observations appear to have been the reports of botanists not familiar with rubber and its significant physical properties. The didactic pattern of conventional reports includes acetone-soluble and benzene-soluble fractions of the dried plant material. Leaves, stems, roots, and whole plant are frequently reported separately, but rarely is any comment made concerning the quality of the rubber. Infrequently, water-soluble fractions are noted.

The concept of rubber in a physical state suitable for commercial use is one that deserves emphasis in relation to the derivation of rubber from domestic plants. Nearly all commercial grades of rubber have been derived from latex

and, as a consequence, have retained as constant ingredients some of the serum components. These components in rubbers formed by coagulation as well as by evaporation (spray-drying, smoke treatment, etc.) influence the behavior of rubber in both the processing and vulcanizing operations, and modify its solubility in organic solvents.

Crude rubber is not completely soluble in benzene and other organic solvents. The rubber recovered from solution either by evaporation or by precipitation (with alcohol or acetone, for example) will not have properties equivalent to the original sample. Midgley[15] and other investigators proposed refined techniques based on differential solubility as evidence that rubber hydrocarbon is in reality a mixture comprising more than one component.

The benzene extract following acetone extraction of plant material may include unsuspected nonrubber ingredients. In one recent example the benzene extract was green; the analyst then tested with acetone, in which the extract proved quite soluble.

The analytical determinations of rubber in plant material need to be standardized so that the results are accurate and not misleading. A committee appointed at the Eastern Regional Research Laboratory in July is actively at work on this problem.

Nearly always the presence of rubber in the latex secreted by plants can be detected by rubbing out a sample between two fingers. If, on coagulation, the latex forms a cohesive ball, the elastic property (high elongation with rapid recovery) is an index of fairly high quality. Failure to form a ball, stickiness, or adhesion to the finger conversely is evidence of the predominance of nonrubber ingredients. Rubber is peculiar in respect to cohesion and speed of recovery. If in Nature it is present but contaminated with a high percentage of other impurities, it is not likely to display its dominant properties. The rubbing test supplemented by routine coagulation with reagents and an examination of the coagulum for cohesion and elasticity is recommended for botanists who wish to check the results of chemical analysis. The ultimate evaluation of rubber must depend on the test of the vulcanized sample. For this purpose a reasonably large sample representative of some proposed method of recovery is needed. A one-pound sample is suggested. Certain laboratories, however, are equipped to make dependable evaluations on smaller amounts[16].

If the factors favoring cultivation of a particular plant and the physical data on tests of vulcanized samples prove favorable, it is important that large quantities of the rubber be prepared by a process suitable for practical operations. Samples of at least 100 pounds are needed for adequate tests to qualify the rubber for large-scale use. Such tests are probably most effectively conducted by the technologists of the rubber industry.

In the government program the selection and approval of a particular domestic source of rubber come under the Bureau of Plant Industry. Operations involving the collection of seed, procurement of suitable land, and planting, cultivation, and harvesting of crops come under the Forest Service. The investigation and approval of processes for obtaining rubber from harvested plant material come under the Bureau of Agricultural Chemistry and Engineering. The procedure is not so simple as this when plantings are undertaken in our sister republics, for then a number of other government agencies must be recognized. The Board of Economic Warfare occupies a key position in establishing such projects.

## *CRYPTOSTEGIA* RUBBER

The number of domestic succulent plants which bear latex is legion. They have aroused the curiosity of thousands of patriotic citizens eager to see them put to use. Obviously, crops of all these species cannot be planted, and a careful discriminating selection must be made on merit.

Among the common varieties of plants which produce latex are the dozens of different milkweeds, the leafy spurge, the wild lettuce, the Indian hemp or dogbane, and many less well-known varieties. It may be of interest to relate the story of one of these plants which is not so familiar, but which is being investigated actively as a promising source of rubber—the asclepiad twiner, *Cryptostegia grandiflora*. It has been grown in Florida, Texas, Arizona, and California. In western Mexico where it is known as *estrella d'espana*, *clavel d'espana*, or *clavel aleman*, the plant grows wild, covering fences and other supporting structures with abundant leafy growth.



Plant of the Russian dandelion, *Kok-saghyz*.

Cryptostegia was introduced into the West Indies by Dolley[17] who had become interested in its rubber-producing possibilities through contacts in western Mexico. Dolley described the habit of growth and the possible yields of rubber from this plant which he estimated to be as high as 400 pounds per acre. At one time rubber was produced from cryptostegia plants in Madagascar and India marketed as *palay* or *pulay*. Samples were displayed at the exposition of Madras as long ago as 1856.

During 1942 the author made observations of cryptostegia growing in the Coachella Valley near Indio, California, at the Government's Acclimatization Station at Bard, California, and at Brownsville, Texas.  Samples of plant material have been received from W. O. Kohler, Spring Valley, California, and from the Government's Plant Introduction Station at Coconut Grove, Florida. Samples of latex have been supplied by E. T. Hermann, Thermal, California, and by the George C. Warner Laboratories at Pasadena.  Warner's original plant material was reported to have come from lower California.  Through the courtesy of Ernest Anderson, University of Arizona, a sample ball of latex rubber from Sinaloa, Mexico, was submitted for examination.  The source plant was identified by J. J. Thornber, Botany Department, University of Arizona, as *C. grandiflora*.  Chemical analyses are given in Table I.

### TABLE I

#### CHEMICAL ANALYSIS OF SOLID RUBBERS

| Source of latex | Ash (percentage) | Acetone extract (percentage) | Acid no. of acetone extract | Water extract (percentage) | Nitrogen (percentage) | Total solids by evaporation (percentage) |
|---|---|---|---|---|---|---|
| Warner Lab. | ... | ... | ... | ... | ... | 31.6 |
| Total solids | 6.45 | 7.4 | 45 | 22.5 | 0.76 | ... |
| Coagulate A | 0.62 | 10.8 | 27 | 1.1 | 0.72 | ... |
| Natural clot | 1.64 | 10.1 | 11 | 1.3 | 0.75 | ... |
| Coachella (Hermann) | | | | | | |
| At 50° C | ... | ... | .. | ... | ... | 16.6 |
| At 105° C | ... | ... | .. | ... | ... | 15.9 |
| Total solids | 9.2 | 8.3 | .. | ... | 3.26 | ... |
| Natural clot | ... | ... | .. | ... | ... | 30.6 |
| Sinaloa ball (Anderson)[a] | 2.05 | 3.73 | 13.6 | 0.35[b] | 0.70 | ... |

[a] Heat loss at 51° C, 8.2%.
[b] 1.33 by Dekker's method.

One is impressed with the prevalence of latex in all parts of this plant, particularly in the fresh shoots.  The latex coagulates readily on rubbing, and forms a coherent ball of tough resilient rubber.  Examination of the latex sent by Hermann revealed a natural clot which contained 30.6 per cent rubber. On dilution with distilled water, the uncoagulated latex immediately coagulated.  The latex responded slightly acid to litmus.  Dilution with sodium chloride solution (around 5 per cent) prevented coagulation and permitted examination of particle size which ranges from 1.5 to 0.2 micron (average, 0.6 to 0.7).  The distribution is uniform, and the particles resemble those of *Hevea* latex in that they have, for the most part, a tear-drop shape.

The sample of latex supplied by the George C. Warner Laboratories was received in good condition except for a natural clot weighing 41 grams when dry and amounting to 35 per cent of the total rubber originally present in the latex.  Data on this latex as received are pH 4.3 by glass electrode, total solids by evaporation 31.6 per cent, dry rubber content by coagulation 21.5 per cent.

COAGULATION OF LATEX.—By the addition of a coalescence agent, following a technique developed in our Malayan research laboratories, it was possible to coagulate this latex when the pH was raised to between 5.8 and 7.0.  As a coalescence agent, 0.5 per cent of Ivory soap solution was used.  The coagulum

resulting from this treatment after washing and drying is referred to as co-agulate A.

VULCANIZATION AND TENSILE TESTS.—Mixing was done according to B. S. Garvey's small-scale technique. Press-cures are indicated in Tables II and III; strips averaged 0.025 inch thick. Tensile tests were made on dumbbell

### TABLE II
#### VULCANIZATION TESTS

| Cure (min.) | Total solids | | | Coagulate A | | | Natural clot | | |
|---|---|---|---|---|---|---|---|---|---|
| | Tensile (lbs. per sq. in.) | Elongation (percentage) | Percentage set | Tensile (lbs. per sq. in.) | Elongation (percentage) | Percentage set | Tensile (lbs. per sq. in.) | Elongation (percentage) | Percentage set |
| | | | | Recipe: rubber 100, sulfur 10; cured at 298° F | | | | | |
| 30 | Undercured | | .. | 200 | 1060 | 25 | Undercured | ... | .. |
| 60 | Undercured | | .. | 340 | 960 | 12 | 100 | 660 | 9 |
| 90 | Undercured | | .. | 1400 | 1130 | 14 | 550 | 960 | 14 |
| 120 | No break at 1020% | | 20 | 1900 | 1060 | 12 | 290 | 870 | 14 |
| 150 | Faulty test-piece | | .. | 260 | 360 | 4 | 490 | 640 | 8 |
| 180 | Faulty test-piece | | .. | Faulty test-piece | | .. | 240 | 420 | 4 |
| | A.C.S. Recipe: rubber 100, ZnO 6, sulfur 3.5, mercaptobenzothiazole 0.5, stearic acid 0.5 (+4.5 parts stearic acid extra to allow for natural deficiency); cured at 260° F | | | | | | | | |
| 20 | 470 | 470 | 56 | Faulty test-piece | | .. | 1800 | 1080 | 25 |
| 40 | 1050 | 660 | 57 | 700 | 800 | 12 | 2580 | 1040 | 21 |
| 60 | 1230 | 740 | 48 | 2730 | 900 | 16 | 2310 | 910 | 60 |
| 80 | 1040 | 580 | 44 | 3730 | 880 | 35 | 3060 | 850 | 24 |
| 100 | 3100 | 830 | 28 | 3175 | 830 | 23 | 1490 | 820 | 53 |
| 120 | 1425 | 880 | 44 | 3620 | 800 | 30 | 2970 | 790 | 28 |

### TABLE III
#### TENSILE TESTS ON SINALOA BALL BY GARVEY METHOD[a]

| Cure (min.) | Tensile (lbs. per sq. in. at: | | | Break | | Permanent set[b] (percentage) |
|---|---|---|---|---|---|---|
| | 500% | 600% | 700% | Tensile (lbs. per sq. in.) | Elongation (percentage) | |
| | | Recipe: rubber 100, sulfur 10; press-cured at 298° F | | | | |
| 90 | 120 | 150 | 200 | 280 | 800 | 7 |
| 120 | 150 | 220 | 320 | 1940 | 1080 | 22 |
| 150 | 280 | 390 | 490 | 2950 | 1010 | 25 |
| 180 | 350 | 480 | 630 | 3250 | 950 | 27 |
| | Recipe: rubber 100, zinc oxide 3.5, sulfur 3.0, mercaptobenzothiazole 0.5, stearic acid 0.5 (+ added 4.5); press-cured at 260° F | | | | | |
| 20 | ... | ... | ... | Too soft to test | | .. |
| 40 | 150 | 200 | 300 | 1580 | 1050 | 22 |
| 60 | 275 | 375 | 730 | 2510 | 940 | 20 |
| 80 | 290 | 400 | 960 | 2660 | 860 | 18 |
| 100 | 375 | 560 | 1180 | 3550 | 880 | 22 |
| 120 | 450 | 1190 | 2310 | 3970 | 800 | 27 |

[a] Garvey method employs a 10-gram batch of rubber and utilizes tensile strips 1 inch between marks and 0.025 inch thick.
[b] Permanent set after 10-minute rest on broken tensile strips.

strips with a Scott compensated-head machine at a jaw separation of 20 inches per minute.

The whole rubbers derived from cryptostegia latex were boardy; those made by coagulation and washing resembled pale crepe. The ash and water-soluble fractions are consistent with the observed difference between dry rubber content, 21.5 per cent, and total solids, 31.6 per cent.

The percentage acetone extracts are intermediate between those of *Hevea* and guayule rubbers. The acid numbers of the acetone extract are much lower than are those for the better grades of natural rubber; the percentages of nitrogen are higher. The influence of acid deficiency is to retard rate of cure, which can be compensated by additional organic acid or other activating agent in the recipe.

The x-ray interference patterns (Figure 1) for *Cryptostegia* rubber and normal *Hevea* rubber are very similar, confirming McGavack's studies[1]. This latex resembles *Hevea* in the size and shape of the particle, ease of coagulation, and high quality of the coagulum, as revealed by the physical tests on vulcanized samples and by hand tests of both cured and uncured rubbers.
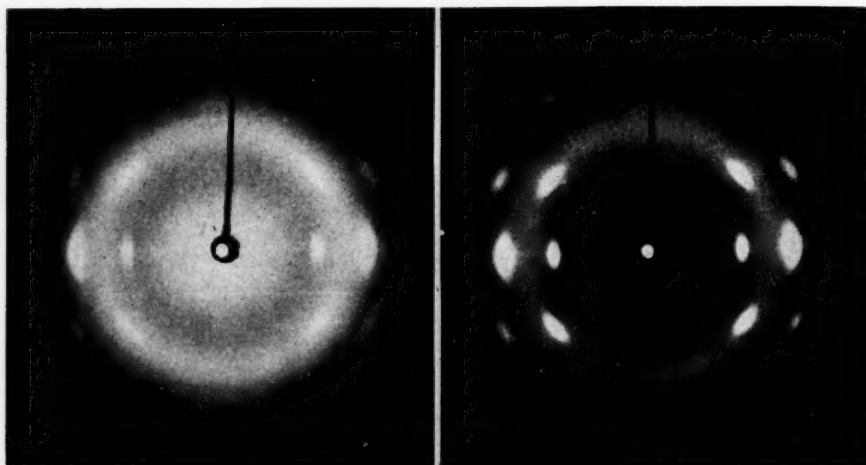


Fig. 1.—X-ray interference patterns for Cryptostegia latex (left) and for smoked sheet.

There is good evidence that a field of this perennial vine might tolerate repeated harvest of the succulent tips as many as thirty times during the growing season. Its abundant twin pods resembling those of milkweed (*Asclepias syriaca*) bear hundreds of seeds which remain viable after months of storage. *Cryptostegia* grows in a variety of locations, and is reported to stand temperatures as low as 18° F, which limits its northern range of growth.

In May and June, 1942, as a result of the above studies, the author recommended to government agencies the extensive planting and further study of this crop. Independently of the above investigation, McGavack also recommended it in his report to the Government. The collection and planting of seed has already been acted upon favorably by the Board of Economic Warfare, and extensive field plantings in about a dozen selected locations here and in our sister republics of North America are being inaugurated. The field nursery of the U. S. Rubber Company at Yuma, Arizona, in charge of R. E. Beckett, who has had years of experience in the introduction of plants, provided McGavack with facilities to make important studies on the tapping cycle of the plant with alternate rest and tapping periods. His results indicate that the plant reacts by what is termed "wound response" to store up larger than normal concentrations of rubber near the wounded region. This study

gives timely data to those who will have to decide on the methods of cultivation and harvesting of the plants. McGavack is continuing to study the minimum age of the plant at which the collection of rubber can be undertaken, and has already performed numerous experiments on the recovery of rubber from the vine. He favors a field crop planted with horizontal wire mesh supports and a harvester to cut the fresh shoots once about every three days, operating like a hedge trimmer or lawn mower. The tips, preferably cultivated to assume an upright posture after trimming, will retain the coagulum of the previous tapping and supply additional fresh latex when again cut about 0.75 inch lower. The method favored by McGavack to free the rubber from most of the associated plant tissues is reminiscent of the reclaiming processes, digestion in dilute acid or alkaline solutions.

The work in our laboratory with shipments of the succulent vine has shown that the latex clots fairly easily when left exposed to air. *C. grandiflora* latex remained stable in the presence of anticoagulant salt solutions. The freshly cut stems of vines which had been shipped from California a week or ten days before, when dropped into anticoagulants, gave up their latex slowly by bleeding. The hybrid cryptostegia from Florida required an adjustment in the strength of the anticoagulant, as its latex is more readily clotted than that of *C. grandiflora*.

The research men from our laboratories in Kuala Lumpur, who have long experience in judging the peculiarities of freshly tapped latex, hold the view that dilute stable latex could thus be produced from freshly cut vines of this plant. The methods of centrifugation to concentrate the latex and of coagulation, washing, and sheeting to form low-serum rubbers are both suggested by our limited observations which require further investigation.

Freshly harvested vines have not been available in our studies, but such experiments as we have been able to run in Akron augur unfavorably for expressing the latex along with plant juices by squeeze rolls or similar devices. The rubber remains in the bagasse, not in the liquids expressed from the plant. Whether the freshly harvested plant protected by anticoagulant solutions can be handled by such machinery without coagulation remains to be proved.

The drying of harvested cryptostegia vines, or other succulent plants which bear latex, to prepare the rubber for comminution and flotation processes as in the case of guayule shrub, remains to be investigated.

The retting of succulent plant material is also deserving of further study. If, for example, a retting operation could be made successful by as simple a technique as the forming of compost piles and, after natural fermentation, the effective processing of the residual rubber, a number of the commoner wild latex bearers might become the source of commercial rubber.

Extraction of rubber from dried plant material with benzene or other organic solvents is not recommended because of the deteriorating effect of solvent on the resulting rubber and the messiness of the operation.

Pilot-plant investigations probably constitute the most important field for immediate study. Successful methods for handling plants like cryptostegia are almost certain to bring to light means for processing the dandelions, milkweeds, spurges, wild lettuce, and dogbanes, some of which abound in nearly every highway, neglected field, and wood lot.

Extensive planting of these common weeds at present scarcely deserves serious consideration. We must first know how to process the crops to make them yield rubber. With this knowledge available, collecting stations for wild plants could easily be organized in thousands of local communities, but we

must avoid at present misdirecting effort and wasting our transportation facilities.

It is therefore prudent to spend time and effort primarily on the more important technical and scientific phases of this program and let the facts garnered in our study designate the course of action.   The ungrudging collaboration of hundreds of scientists in this common undertaking is a favorable sign for the early solution of the difficult problems which confront us.

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# THE INTERACTION BETWEEN RUBBER AND LIQUIDS

## III.  THE SWELLING OF VULCANIZED RUBBER IN VARIOUS LIQUIDS *

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The swelling of vulcanized rubber in a wide range of liquids has been studied by Whitby and coworkers[1], and a number of interesting regularities have been pointed out.  It has been suggested[2] that a relation should exist between the swelling power of a liquid for rubber and its cohesive energy density.  The purpose of the present paper is to develop this idea a little further, and to show how it can be used to interpret Whitby's data.

It has already been pointed out[3] that the swelling and dissolution of raw rubber is best considered as the problem of the miscibility of two liquids. Vulcanized rubber differs from raw rubber essentially in that it possesses a structure which cannot be broken down completely by any solvent; the material therefore swells but cannot be dispersed unchanged[4].  To describe this behavior thermodynamically, we require to know the partial molar entropy $\Delta S_0$ and heat $\Delta H_0$ of swelling of the rubber by liquid.   No thermodynamic study has yet been made of the system: vulcanized rubber + liquid, but it is reasonable to assume that vulcanized rubber will differ from raw rubber only when a considerable amount of liquid has been imbibed.   This is confirmed by the very similar swelling of raw and vulcanized rubbers in liquids of not too great swelling power.   At low solvent concentrations, $\Delta S_0$ is therefore taken to have the values found for raw rubber + benzene[5].   As before[3], we assume $\Delta S_0$ to be the same for all liquids, and seek to explain their different swelling powers in terms of their heats of swelling.   Clearly—if we neglect any liquids which may evolve heat on swelling—the maximum degree of swelling will be found when $\Delta H_0 = 0$.   Since the condition for equilibrium between swollen rubber and pure liquid is that the Gibbs free energy of swelling $\Delta G_0 = 0$, it follows that, for the best swelling agent, the equilibrium condition may also be written: $\Delta S_0 = 0$.   Whitby's data[1] suggest a maximum swelling $Q$ of approximately 5 (cc. liquid/cc. rubber) and we therefore take $\Delta S_0 = 0$ when $v_0$ (vol. fraction of liquid) $= 0.833$.   One other point on the entropy curve for vulcanized rubber is obtained by making the further assumption that the heat of swelling of vulcanized rubber by benzene is the same as that of raw rubber. Taking $Q = 3.94$ for the maximum swelling of benzene[6], we calculate from our previous data[5] that $\Delta H_0 = T\Delta S_0 = 2.6$ cal. per mole at $v_0 = 0.798$.   These three conclusions about the entropy of swelling have been combined, as shown in Figure 1, in which $\dfrac{T\Delta S_0}{(1 - v_0)^2}$ is plotted as a function of $v_0$ for raw and vulcanized rubber.   The curve for the latter is drawn through the above two points so as to merge with the curve for raw rubber in benzene at low values

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of $v_0$.  It is clear that the resulting curve is only a first approximation and that it applies only to the specimen of vulcanized rubber used by Whitby[7].

We have now to consider how the heats of swelling of rubber by various liquids may be related to some known property of the liquids.  The heats of mixing of most normal liquids are related to the difference between their cohesive energy densities[8] by an equation of the form:

$$\Delta H_0 = kV_0\left\{\sqrt{\frac{E_0}{V_0}} - \sqrt{\frac{E_1}{V_1}}\right\}^2 (1 - v_0)^2 \tag{1}$$

where $\Delta H_0$ is the partial molar heat of dilution of the mixture (composition $v_0$) by liquid$_0$, $V_0$ and $V_1$ are the molar volumes of the liquids, and $E_0$ and $E_1$ are the molar cohesive energies of the liquids.  According to the simple theory, $k = 1$; but larger values are usually found experimentally, even for mixtures of hydrocarbons[9].  Values of $E_0$ are obtained from $E_0 = L_0 - RT$, where $L_0$ is the molar latent heat of evaporation, and is to be calculated from the tem-
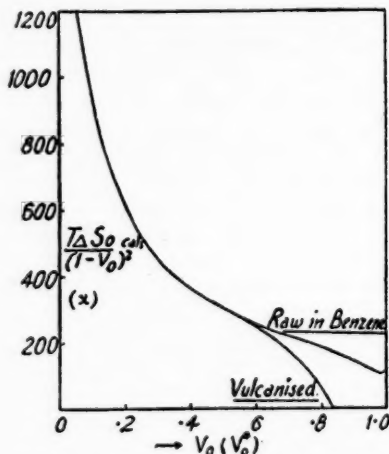


FIG. 1.—Entropy of dilution of rubber by liquids.

perature coefficient of the vapor pressure at the temperature $T$ ($= 298°$ K). Precise values of $E_0$ are known for very few liquids, so that

$$\left\{\sqrt{\frac{E_0}{V_0}} - \sqrt{\frac{E_1}{V_1}}\right\}^2$$

is subject to large uncertainties.  If we assume Equation (1) to apply to swelling of vulcanized rubber, where the subscript $_1$ is taken to denote rubber, it is evident that $\sqrt{E_1/V_1}$ must be treated as a constant $\alpha$, independent of the nature of the liquid, and having a value of the order 8 (cal. per cc.)$^{0.5}$ to bring it in line with known $\sqrt{E/V}$ values for hydrocarbons[8]; $k$ may be regarded as an adjustable parameter, but must be of the order of magnitude of unity.

The condition for the equilibrium swelling of vulcanized rubber in a liquid$_0$ is now written: $T\Delta S_0 = \Delta H_0$, or:

$$\sqrt{\frac{x}{V_0}} = \sqrt{k}\left(\sqrt{\frac{E_0}{V_0}} - \alpha\right) \tag{2}$$

where

$$x = \frac{T\Delta S_0}{(1 - v_0{}^*)^2} \tag{3}$$

and $v_0{}^*$ is the volume fraction of liquid when the rubber is fully swollen by that liquid. Figure 1 gives directly $x$ as a function of $v_0{}^*$ for a series of liquids, and it is evident from Equation (2) that $\sqrt{x/V_0}$ should be a linear function of $\sqrt{\dfrac{E_0}{V_0}}$. Whitby's data give $Q$ and therefore $v_0 \left( = \dfrac{Q}{1 + Q} \right)$, so that they can be used to test the validity of Equation (2). The results are shown in Figure 2,
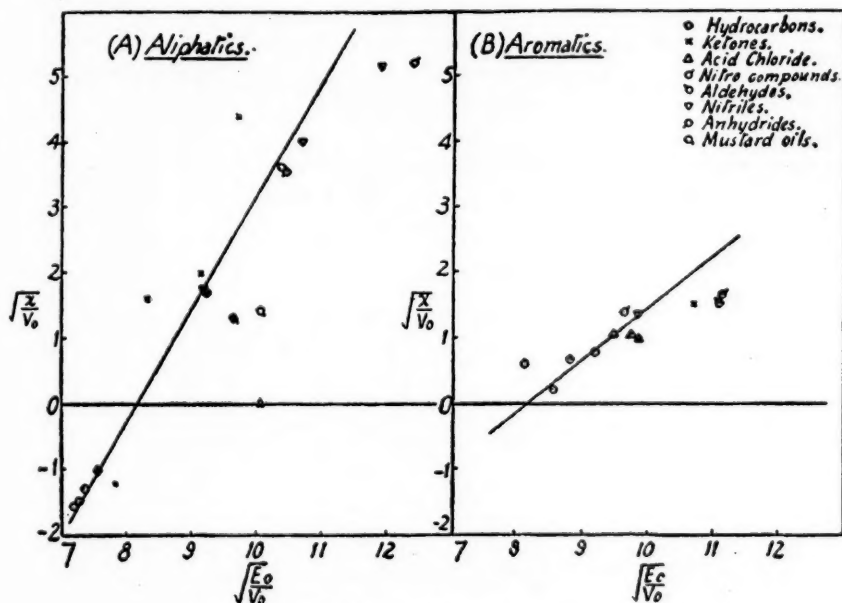


FIG. 2.—Entropy of dilution as a function of cohesive energy.

which includes the whole of Whitby's data on liquids for which $E_0/V_0$ could be calculated, with the exception of the alcohols and acids. These are omitted, since it is clear that the above theory cannot be expected to apply to such highly associated liquids. It is evident that Equation (2) does not hold precisely for the whole range of liquids examined, but the more normal aliphatic liquids lie reasonably well on a line. Indeed, bearing in mind the uncertainties both in $Q$ (and therefore in $x$) and in $E_0/V_0$, the agreement must be regarded as satisfactory. Whitby has very kindly allowed me to examine his unpublished data covering a further series of liquids. Few of these have known cohesive energies, but the line drawn in Figure 2a is in good agreement with his results for some simple esters, for ethyl ether and for isobutylamine. It may, therefore, be taken as representative of the normal behavior of aliphatic liquids, and a special explanation must be sought for any large deviation from it. The constants given by this line are of the expected order: $\alpha = 8.15$, $k = 3.0$, the former giving a cohesive energy density for rubber of 66 calories

per cc. Whitby has pointed out[1] that aromatic liquids show much larger swelling than aliphatic compounds containing the same polar group. It is now found that the swelling is also larger at a given $E_0/V_0$. This difference may arise either from a different entropy or a different heat of swelling, or both. Having assumed $\Delta S_0$ to be the same for all liquids, the whole of the discrepancy has to be ascribed to $\Delta H_0$. In Figure 2b it is seen that Equation (2) holds quite well for aromatic liquids, with the same value of $\alpha = 8.15$, but giving this time $k = 0.65$. There is as yet no experimental evidence as to the validity of this method of separating aliphatic and aromatic compounds.

It is now possible to calculate the swelling power $Q$ of a liquid from its cohesive energy and molecular volume, from the expression:

$$x = kV_0\left\{\sqrt{\frac{E_0}{V_0}} - 8.15\right\}^2 = f(Q) \tag{4}$$

where $k = 3.0$ for aliphatic, 0.65 for aromatic liquids, and $x = f(Q)$ is defined by Figure 1. In Figure 3 (A) and (B), the lines drawn give values of $Q$ calcu-
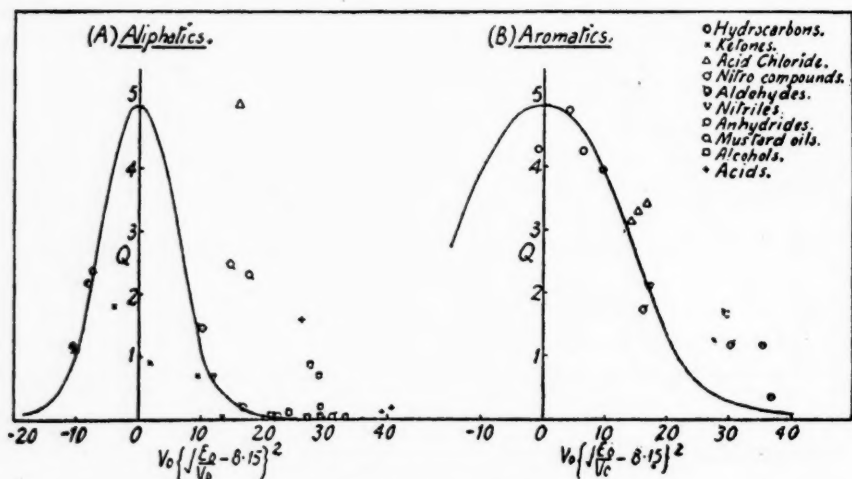


Fig. 3.—Swelling as a function of cohesive energy.

lated in this way as functions of $V_0\{\sqrt{E_0/V_0} - 8.15\}^2$, while the points show the extent of the agreement with experiment. On the whole, this is considered satisfactory, especially when we note the sensitivity (except for small $Q$) of $Q$ to small errors in $x$. It is clear that there is at least a close correlation between $Q$ and $V_0\{\sqrt{E_0/V_0} - 8.15\}^2$. This is all that would be expected from this treatment.

The causes of some of the major discrepancies may now be briefly considered. Most striking is the anomalously high swelling power of acids and alcohols, which undoubtedly arises from their high degree of association. The full effect of the polar group is not shown, since the liquids tend to remain associated, even when present in quite low concentration in the rubber[10]. Whitby's unpublished data show that chlorinated hydrocarbons also possess high swelling powers, and here the explanation probably lies in a smaller $\Delta H_0$

than would be calculated from the cohesive energy. It is well known that chlorinated hydrocarbons (especially $CHCl_3$) tend to show negative, or only slightly positive, values of $\Delta H_0$ on mixing with a wide range of liquids, including hydrocarbons.

## SUMMARY

The entropy of swelling of vulcanized rubber is estimated, and assumed independent of the nature of the swelling liquid. The heat of swelling is related to the cohesive energy of the liquid, and a value of 66 calories per cc. deduced for the cohesive energy density of rubber. The swelling power of a liquid can be calculated approximately if its cohesive energy and molecular volume are known. Substantial agreement with theory is found in most cases, although it is necessary to consider aliphatic and aromatic liquids separately. The anomalously high swelling power of acids and alcohols arises from their association.

## ACKNOWLEDGMENT

## REFERENCES

[1] Whitby, Evans and Pasternack, *Trans. Faraday Soc.* **38**, 269 (1942).
[2] Gee, *Trans. Faraday Soc.* **38**, 282 (1942).
[3] Gee, *Trans. Faraday Soc.* **38**, 276 (1942); Flory, *J. Chem. Physics* **10**, 51 (1942).
[4] Examples quoted by Whitby of the ultimate dissolution of vulcanized rubber must be ascribed to degradation, probably oxidation, unless evidence can be brought to show that the vulcanized rubber can be recovered unchanged from solution.
[5] Gee and Treloar, *Trans. Faraday Soc.* **38**, 147 (1942).
[6] Whitby's data do not give any equilibrium values of $Q$. If the present theory is correct, there must be a definite limit to swelling, and our experience suggests that, for the small specimens used by Whitby, equilibrium would be attained within a day or so. We therefore accept Scott's suggestion (cf. *Trans. Faraday Soc.* **38**, 284 (1942)) that further swelling is spurious, arising most probably from oxidation, and estimate equilibrium values of $Q$ by extrapolating $Q$ roughly to $t = 0$. Values obtained in this way are used throughout this paper.
[7] The heat and entropy of dilution of raw rubber by benzene used in deriving Figure 1 differ somewhat from those given previously (cf. Scott, *Trans. Faraday Soc.* **38**, 284 (1942)), owing to the correction of the latter for the departure of benzene vapor from perfect gas behavior. Employing the correcting factors of Eucken and Mayer (*Z. physik. Chem.* [B] **5**, 452 (1929)), the Gibbs free energy of dilution remains substantially unchanged, but the heat of dilution is considerably reduced. The revised values can be represented by

$$\Delta H_0 = 78\Delta h_0 = 156 \left( \frac{W_r}{1.7 - 0.7 W_r} \right)^2$$

where $W_r$ is the weight fraction of rubber. This equation has been used in place of Equation 20 in the work of Gee and Treloar (*Trans. Faraday Soc.* **38**, 147 (1942)). The conclusions drawn there are, of course, unchanged by the correction.
[8] Hildebrand, "Solubility", Reinhold Publishing Corp., New York, 1936, p. 73; Scatchard, *Chem. Rev.* **8**, 321 (1931); *J. Am. Chem. Soc.* **56**, 995 (1934).
[9] Scatchard, *J. Phys. Chem.* **43**, 119 (1939).
[10] This behavior is shown very strikingly by a thermodynamic study of the system: rubber + methanol, which has been carried out by L. R. G. Treloar. The results will be described in a subsequent paper of this series.

# INTERMOLECULAR FORCES AND MECHANICAL BEHAVIOR OF HIGH POLYMERS *

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In order to connect the mechanical properties of high polymers with their fundamental architecture, several structural characteristics must be considered. There is, first, the average molecular weight or the average polymerization degree of the substance[1], which varies between 20,000 and 1,000,000 or between 100 and 5000, respectively. There is the chain-length distribution curve[2], which describes the heterogeneity of the material, and is comparatively narrow in some cases and fairly wide in others. There is the chemical nature of the monomer, which can be a hydrocarbon, an alcohol, ester, ether, amine, acid, nitrile, etc., so that the polymer can have very different chemical characteristics. There are, finally, the intermolecular forces between the chain molecules, which are a consequence of the chemical nature of the monomer, and which, together with the flexibility of the chains, have a preponderant influence on mechanical performance.

This article will discuss the influence of each of these structural features on the physical properties of different high polymers, built up mainly of straight or moderately branched chains. Typically thermosetting resins and strongly vulcanized elastometers, which are highly branched and cross-linked, are not included, because their complex three-dimensional framework warrants additional description, which is still the subject of divergent points of view[3]. An approximate picture of the situation is given in Table I, which shows the

### TABLE I

#### CONNECTION BETWEEN PROPERTIES AND STRUCTURAL CHARACTERISTICS[a] OF HIGH POLYMERS

| Property | Average polymerization degree | Branching | Cross-linking | Homo-polar nature | Hetero-polar groups | Flexibility of chains | Readiness of chains to crystallize | Orientation of crystallites |
|---|---|---|---|---|---|---|---|---|
| Modulus of elasticity | + | ? | + | ? | ? | − | + | + |
| Ultimate tensile strength | + | ? | ? | − | + | ? | + | + |
| Ultimate impact strength | + | ? | − | + | + | + | + | − |
| Elongation to break | + | ? | − | + | ? | + | − | − |
| Range of elastic extensibility | + | − | − | + | + | + | ? | ? |
| Tendency to contract | + | ? | − | − | − | + | − | ? |
| Surface hardness | + | ? | + | − | + | − | + | + |
| Resistance to temperature | + | ? | + | + | + | − | + | ? |
| Electric resistance | ? | ? | + | + | − | ? | ? | ? |
| Dielectric sonstant | ? | ? | ? | − | + | ? | ? | ? |
| Resistance to swelling | + | + | + | ? | ? | − | + | + |
| Resistance to moisture | + | + | + | ? | ? | ? | + | + |
| Resistance to acids | ? | ? | + | + | ? | ? | + | ? |
| Resistance to alkalies | ? | ? | + | + | ? | ? | + | ? |
| Adhesive power | ? | + | − | ? | + | + | − | − |

[a] A plus sign means that the structural feature increases the property under consideration; a minus sign means that it decreases it. A question mark indicates that we do not know how the property is affected by the structural characteristic.

connection of some properties of high polymers with structural characteristics such as average polymerization degree[4], branching, cross-linking[5], intermolecular forces[6], etc.

## EFFECT OF AVERAGE POLYMERIZATION DEGREE ON MECHANICAL PROPERTIES

The connection between mechanical properties and average chain length has been frequently investigated. Early work was done by Carothers[7], Clibbens and Ridge[8], Davidson[9], Ohl[10], Ott[11], and Rocha[12]. Recently this question was more thoroughly studied by Douglas and Stoops[13] and coworkers[14], Spurlin[15], and Straus and Levy[16]. The general result is that, to obtain any mechanical strength, a certain minimum degree of polymerization is necessary. This critical minimum value ranges between 40 and 80. It seems to be smallest in the case of Nylon or proteins, and largest for polyhydrocarbons, such as polythene and polystyrene. As soon as this critical value of chain length is surpassed, the material starts to show mechanical strength, and its ultimate tenacity increases roughly in proportion to the average degree of polymerization. Figure 1 is a diagram of this situation. The circles at the left of the shaded area represent polyamides; the crosses at the right denote polyhydrocarbons. All other straight-chain high polymers, such as cellulose esters, polyvinyl derivatives, etc., lie in between. The proportionality between mechanical strength and chain length holds until polymerization degree reaches about 250. Then the curve bends down gradually and, after a polymerization degree of 600 or 700, the ultimate strength does not depend on chain length appreciably.
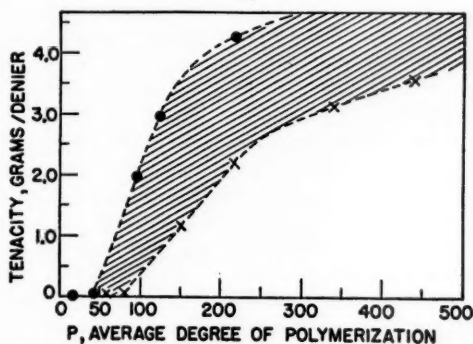


Fig. 1.—Effect of average degree of polymerization on tenacity of high polymers.

The slope of the curves of Figure 1 seems to depend not only on the nature of the high polymer but also on the type of spinning or casting used to prepare the sample. If crystallization and orientation are favored during spinning, moulding, or casting, a higher level of mechanical strength is reached sooner than if the conditions are such that the material is left in a more disordered state. However, once the spinning conditions are established, Figure 1 gives a reasonable picture of how the average chain-length influences mechanical properties.

## DISTRIBUTION CURVE AND MECHANICAL PROPERTIES

While the influence of average polymerization degree on mechanical strength is fairly well established and can, with some justification, be represented in a curve like Figure 1, the influence of chain length distribution is still an unsolved problem. Recently, promising attempts have been made by Dolmetsch and Reinecke[17], Eisenhut[18], Harris and coworkers[14], Schieber[19], Mark and

Simha[20], and others to establish a connection between the distribution curve and the characteristic mechanical properties of high polymers. Their work seems to indicate the following results: The shape of the distribution curve seems to have no definite effect on the ultimate strength except that a comparatively small amount (between 10 and 15 per cent by weight) of components having a polymerization degree below 150 are definitely detrimental to the mechanical properties of the sample.

### CHEMICAL NATURE, INTERMOLECULAR FORCES, AND MECHANICAL PROPERTIES

The chemical nature of the monomer and the way in which the monomers in each individual chain are linked together seem to have an important influence on the mechanical behavior of the material. The investigations of the last two decades indicate that high polymers in general have a rather intricate two-phase or even multiphase nature.

Certain areas of a given sample exhibit a high degree of internal geometrical organization. One usually refers to them as crystallites or micelles. In fact, they have many properties commonly found in crystals. They diffract x-rays and electrons of medium wave length, so regular fiber or powder diagrams are produced. They exhibit birefringence, and show distinct anisotropy in swelling[21]. In other respects, however, these crystallized areas are unlike the crystals of normal organic substances. They do not have well defined plane boundaries or sharp symmetrical edges. Their sizes seem to vary widely; in some cases, such as proteins or vinyl copolymers, they are very small; normally they are rodlike or ribbonlike and have dimensions between $10^2$ and $10^4$ Å.U. In some cases it has been observed that they grow to comparatively large homogeneous units of dimensions up to $10^5$ or $10^6$ Å.U.[22]

These crystallites in a high polymer should not, perhaps, be compared with the completely shaped and independent individuals of a crystal sugar powder, but rather with the grains of a polycrystalline metal. These grains also show many typical properties of normal crystals (x-ray pattern, birefringence, anisotropy) but, on the other hand, do not have plane boundaries and sharp edges. It seems, in general, that investigators of organic high polymers can utilize with advantage the methods developed for and applied in metallography.

Cellulose crystallites or rubber micelles, then, will be taken to mean small areas of somewhat indefinite size and shape, inside of which the monomeric units are regularly arranged in a three-dimensional periodic pattern.

But high polymers do not consist entirely of such well organized components. They always contain a certain proportion of disordered and randomly entangled chains, which are usually referred to as the amorphous or disordered fractions. Recently Alfrey and Mark[23], Bunn[24], Clark[25], Fuller and coworkers[26], Gehman and Field[27], Harris and coworkers[14], Hermans[28], Kratky[29], Mark[30], Nickerson[31], and Purves[32] have used different methods to learn about these components of a high polymer. It seems that they contain the chains in less perfect arrangement, due to the fact that some irregularity has prevented them from reaching the proper equilibrium positions of the crystallized state. It is the belief[33] that one and the same chain can go through a crystalline area, enter an amorphous portion, go through it, and enter another crystallite. This assumption has the consequence that there is no sharp boundary between the crystallized and disordered areas, but that the chains of a certain crystal become disordered somehow, degenerate into fringes, and finally reach a completely disordered arrangement. Hence it may be appropriate not to make a

sharp distinction between crystallized and amorphous, but to consider various degrees of disorder, just as more than one crystallized modification of different high polymers have been observed. Baker, Fuller, and Pape proposed to consider mesomorphous phases in quenched polyamides, Taylor[34] has repeatedly emphasized that chains with regularly distributed centers of attraction are unlikely to curl up in a completely irregular way.

There seem to be even different degrees of randomness in a substance like rubber, as indicated by its thermal properties, particularly by the existence of a second-order transition point around $-80°$ C, which was established by careful measurements of Bekkedahl and Wood[35]. Transition points of higher order seem to be a rather general feature in high polymers with chains of a certain internal flexibility or foldability, such as polystyrene, polyisobutylene, and polyacrylates. Theoretical considerations about a certain degree of regular folding in amorphous rubber were proposed several years ago by Kirchhoff[36] and by Fikentscher and Mark[37], and were later improved by Mack[38], who even based on them a theory of the elastic properties of rubber[39].

Polystyrene of polymerization degrees between 1000 and 2000 has not yet been forced into a definite crystalline structure by any mechanical or thermal pretreatment, but it shows a distinct transition point around 80° C. According to experiments of Davis[40] and Whyte[41], it exhibits an amorphous x-ray diagram in which sharpness and intensity distribution of the diffuse halo can be effected by appropriate pretreatment.

All this shows that, even in chainlike (or slightly branched) hydrocarbons, where the intermolecular forces are weak and geometrically diffuse, various degrees of disorder exist and contribute to the mechanical behavior of the material[42].

The tendency for a certain regularity in the curled up state seems to be distinctly more pronounced if groups with attractive forces, such as permanent dipoles, easily polarizable bonds, or hydrogen bonding groups, are regularly distributed along the chain. Proteins and polyamides are examples for such systems. Baker, Fuller, and Pape[43] investigated the crystallization of polyamides under different experimental conditions, and Taylor[44] emphasized that certain mechanical properties of polyamides can be better understood if a regular folding of the chains in the quenched state is assumed. In accordance with these considerations, one has to distinguish between the internal crystallization of a single chain and the external crystallization between two different chains. Cold drawing can be visualized as converting internal crystallization (regular curling up of the different individual chains) into external crystallization (parallelization of straightened out chains).

This picture of the conversion of folded up chains having a certain degree of internal regularity into straightened out chains having a higher degree of mutual geometrical organization seems to be one molecular mechanism which accompanies most mechanical deformations of long-chain polymers.

Whether the free energy has its absolute minimum in the initial state (curled up chains) or in the final arrangement of the system (mutual crystallization of the chains) depends on the molecular attraction between the chains, on their geometrical fitting into the crystal lattice, and on temperature and external forces.

1. If the molecular attraction is small and the chains fit badly into a lattice, then, at a given temperature and stress, the material will always have the tendency to return into its original state. Such conditions are typical of rubber.

2. On the other hand, if the forces are strong and the fine structure of the chains provides for easy fitting into a lattice, a state of high external crystallinity is favored and the material is a typical fiber.

3. In intermediate cases, in which the forces are moderate and the geometry of the chains is moderately favorable for crystallization, the behavior of the material will depend greatly on external conditions, such as temperature and external mechanical forces. Such systems are typical plastics.

These qualitative considerations show that rubbers, plastics, and fibers are not intrinsically different materials. Their difference is rather a matter of degree and is produced by the way in which the intermolecular forces between the long chains and their general tendency to curl and fold coöperate in forming a certain mixture of crystallized and disordered portions in the sample.

In general, it can be said that, under given conditions (temperature and external forces), the tendency to crystallize is brought about by two different factors, which are conflicting with each other.

Forces between Chains. This influence corresponds to the $\Delta H$ term in the expression for the free energy change during crystallization. If the forces are strong (above 5000 calories per mole of the group involved), then they will preponderantly dictate the behavior and the material will be expected to be a more or less typical fiber. This seems to be true for cellulose, proteins, Nylon, Vinyon, and Saran.

Geometrical Bulkiness of Chains. This influence corresponds to the $T\Delta S$ term in the expression for the free energy change during crystallization. Chains that fit easily into a lattice (polyethylene, trans-polydiolefins) crystallize under the influence of comparatively weak forces and hence, in general, have a tendency to appear more fiberlike than would be expected if the forces alone were considered. On the other hand, materials which have bulky chains do not crystallize even if the intermolecular forces are quite strong. Hence they will be more rubberlike than one would expect on taking into account only the intermolecular forces (polystyrene, vinyl copolymers, cellulose mixed esters, etc.).

TABLE II

Effect of Intermolecular Forces of Some High Polymers on Mechanical Behavior

| Substance | Covalent bond along chains | Dissociation energy, cal./mole | Groups responsible for attraction | Molar cohesion per 5 Å chain length with coordination no. of 4 in cal./mole |
|---|---|---|---|---|
| Polyethylene | —C—C— | 70-80,000 | (CH₂) | 1000 |
| Polyisobutylene | —C—C— | 70-80,000 | (CH₂), (CH₃) | 1200 |
| Polybutadiene | —C=C— | 70-120,000 | (CH₂), (CH=CH) | 1100 |
| Rubber | —C=C— | 70-120,000 | (CH₂), (CH=CCH₃) | 1300 |
| Polystyrene | —C—C— | 70-80,000 | (CH₂), (C₆H₅) | 4000 |
| Polychloroprene | —C=C— | 70-120,000 | (CH₂), (CH=CCl) | 1600 |
| Polyvinyl chloride | —C—C— | 70-80,000 | (CH₂), (CHCl) | 2600 |
| Polyvinyl acetate | —C—C— | 70-80,000 | (CH₂), (COOCH₃) | 3200 |
| Polyvinyl alcohol | —C—C— | 70-80,000 | (CH₂), (CHOH) | 4200 |
| Cellulose | —C—O—C— | 80-90,000 | (OH), (—O—) | 6200 |
| Cellulose acetate | —C—O—C— | 80-90,000 | (OOCCH₃), (—O—) | 4800 |
| Polyamides | —C—N—C— | 70-90,000 | (CH₂), (CONH)H | 5800 |
| Silk fibroin | —C—N—C— | 70-90,000 | (CHR), (CONH)H | 9800 |

Table II illustrates the possible applicability of this consideration. The first column lists high polymers extending from polyhydrocarbons (having small

intermolecular forces) to proteins and polyamides (having strong forces between the chains). The next column shows the type of covalent bond which links the different monomers in each single chain together. The approximate dissociation energies of such bonds are listed in the next column; they are all above 70,000 calories per mole, which corresponds to a strong primary valence bond. It has been calculated that the force to rupture such links would correspond approximately to a tensile strength of 150 grams per denier, which is far above any experimentally observed value[45]. The highest tenacities of fibers which have actually been measured are around 10 grams per denier. This shows that rupture of the fiber does not preponderantly involve rupture of the individual chains, but rather their slipping along one another and finally breaking of van der Waals bonds.

The fourth column of Table II contains the groups which are mainly responsible for the mutual attraction of the chains as a consequence of the different types of van der Waals forces. In the case of hydrocarbons, the attraction is due to unpolar methyl or methylene groups with cohesive energies of around 1000 calories per mole of the group; in the case of polyamides one has CONH— groups, which are hydrogenbridged from chain to chain and represent a molar cohesion of around 8000 calories per mole.

The forces of all attractive groups accumulate along the chains and provide for a certain molecular cohesion per unit length. The last column of Table II contains the energy values of this cohesion, calculated for a length of 5.0 Å.U., under the assumption that each chain is surrounded by four others (specific molar cohesion). The figures of the last column show that all typical rubbers (natural rubber, Neoprene, polybutadiene, polyisobutylene) have a specific molar cohesion between 1000 and 2000 calories. The only exception is polyethylene, where the forces are also small, but where the rubberlike properties are not specifically pronounced. As already mentioned, this may be explained by an exceedingly good fitting of the straight and comparatively not too flexible zigzag hydrocarbon chains in the crystal lattice.

If the specific molar cohesion as listed in the last column assumes values above 5000 calories, the substances behave typically as fibers with a high modulus of elasticity ($10^{11}$ to $10^{12}$ dynes per sq. cm.) and considerable tensile strength. It seems again that the ease with which a given chain can be arranged in a lattice determines the position of the material among the fibers. Thus, Nylon is generally stronger and tougher than silk, although its specific molar cohesion is smaller.

In cases when the molar cohesion as listed in column 4 is between 2000 and 5000 calories, the material behaves like a plastic; it becomes soft or rubberlike at elevated temperatures but shows crystallization at normal temperatures without stretching. Polyvinyl alcohol, which has particularly smooth chains, shows a tendency to exhibit fiber properties, although according to its intermolecular attraction it should be a typical plastic.

It must be understood that Table II represents only a crude and preliminary attempt to correlate the properties of rubbers, plastics, and fibers from the point of view of intermolecular attraction, because it considers only forces and does not sufficiently take into account the entropy changes during crystallization.

There is not enough experimental material available to extend Table II, but such an extension seems to be possible for polyhydrocarbons.

## STRUCTURE AND MECHANICAL BEHAVIOR OF SOME POLYHYDROCARBONS

To obtain information on how much the internal structure of a chain influences the mechanical behavior of the material, it seems advisable to select a group of substances which are similar in chemical nature and, hence, exhibit intermolecular forces of the same magnitude. At present polyhydrocarbons offer the best chance for such a study, although it must be pointed out that more experimental data are needed. Nevertheless, it may be worthwhile to outline such a comparison (Table III).

*trans*-POLYBUTADIENE.—If butadiene is polymerized with sodium in the gaseous or liquid phase or with a peroxide catalyst in emulsion, materials are obtained which are, for the most part, more or less highly cross-linked, and therefore should not be included in this comparative study. However, by digesting and degrading these materials in solvents, soluble fractions can be obtained which yield samples of more rubberlike properties. In the unstretched state, they show an amorphous diagram. The diameter of the diffuse ring leads to an average chain distance of about 4.6 Å.U. The density of the material is around 0.93. On stretching, fiber diagrams of limited sharpness are obtained, indicating that the material is reluctant to crystallize. As accurately as it can be estimated, the fiber period is around 5 Å.U.

The small fraction of the material which gives the fiber diagram appears to be *trans*-polybutadiene, but the greater part of any given sample is a copolymer of the *cis* and *trans* isomers. Pure *trans*-polybutadiene (No. 1 in Table III) would be a plastic, presumably somewhat harder than gutta-percha, with a melting point around 100° C and a definite tendency to crystallize. The copolymer (No. 7), however, has a strongly reduced crystallizability and therefore shows more rubberlike properties. Apparently the result of the polymerization of butadiene is mainly a *cis-trans* copolymer, with accidental longer pieces of pure *trans* chains, which are parallelized upon stretching and form bundles of some limited internal regularity.

POLYETHYLENE.—The polymerization of ethylene under pressure[46] leads to a polymer called "polythene", which seems to be built up mainly by straight chains. It was thoroughly investigated by Bunn[47] and Fuller[48]. The identity period is 2.53 Å., showing that the chains have the planar zigzag shape as in lower paraffins. The high melting point reflects the easy way in which such straight unsubstituted chains fit into a crystal lattice. The material is, therefore, a plastic rather than a rubber at room temperature.

*cis*-POLYBUTADIENE.—No direct experimental evidence for the existence of this isomer can be given. Apparently, however, it represents a certain part of all samples of polybutadiene.

*α-trans*-POLYISOPRENE.—This substance occurs as a crystalline resin in a tree and is known as α-gutta-percha. Its structure was studied by Hauser and von Susich[49] and Meyer[50], and was thoroughly discussed by Bunn[51]. The *trans* character of the chain structure seems to provide for easy crystallization; the density is high and the material behaves like a plastic at room temperature.

*β-trans*-POLYISOPRENE.—This material is obtained if α-gutta-percha is heated to about 70° C and then cooled rapidly; it is called β-gutta-percha. The structure was worked out by Fuller[48], Meyer[50], and Misch[52], and was recently reinvestigated by Bunn[51]. The chains are straight and fit comparatively easily in a crystal lattice. Hence the material is similar to the *alpha* form in mechanical properties.

## TABLE III
### STRUCTURE AND MECHANICAL BEHAVIOR OF POLYHYDROCARBONS[a]

| Polyhydrocarbon | Remarks | Density in amorphous state | Density in crystalline state | Average distance of chains in amorphous state (Å.U.) | Identity period of crystalline state (Å.U.) | Melting point of crystalline state (°C) | Melting point of crystalline state (°K) | Weight average polymerization degree | Melting process H (cal/mole) | Melting process S (cal/°C/mole) | Mechanical behavior at room temperature |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. trans-Polybutadiene | Not known in pure state | ... | ... | ... | 5.0 | ... | ... | ..... | (310) | (0.82) | ...... |
| 2. Polyethylene | Polythene | ... | 1.29 | 4.3 | 2.53 | 115–25 | 388–98 | 2000–3000 | (300) | 0.78 | Plastic |
| 3. α-trans-Polyisoprene | α-Gutta-percha | ... | 0.95 | 4.6 | 8.9 | 65 | 338 | 1000 | (270) | 0.80 | Plastic |
| 4. β-trans-Polyisoprene | β-Gutta-percha | ... | 0.95 | 4.6 | 4.7 | 56 | 329 | 1000 | (270) | 0.82 | Plastic |
| 5. cis-Polybutadiene | Not known in pure state | ... | ... | ... | ... | ... | ... | ..... | ... | ... | ...... |
| 6. Polyisoamylene | Hydrogenated rubber | ... | ... | ... | ... | ... | ... | Comparatively low | ... | ... | Plastic |
| 7. cis-trans-Copolybutadiene | Buna | 0.93 | 0.96 | 4.6 | ... | ... | ... | ~2000 | ... | ... | Rubberlike |
| 8. cis-Polyisoprene | Rubber | 0.93 | 0.96 | 4.9 | 8.1 | 11 | 284 | 2000–3000 | 270 | 0.96 | Rubberlike |
| 9. trans-Polydimethylbutadiene | Not known in pure state | ... | ... | ... | 5.0 | ... | ... | ...... | ... | ... | ...... |
| 10. cis-Polydimethylbutadiene | Not known in pure state | ... | ... | ... | ... | ... | ... | ...... | ... | ... | ...... |
| 11. cis-trans-Copolydimethylbutadiene | Methyl rubber | ... | ... | 5.4 | ... | ... | ... | Comparatively low | ... | ... | Rubberlike |
| 12. Polyisobutylene | Vistanex | 0.915 | 0.937 | 6.3 | 18.63 | 0 | 273 | 2000–3000 | (270) | 1.0 | Rubberlike |

[a] Most of the figures are taken from the literature; some are the results of recent experiments carried out by A. L. Davis and S. Whyte at Brooklyn Polytechnic Institute.

POLYISOAMYLENE.—This material could be obtained by polymerizing iso-amylene, but it is difficult to lead this reaction to a sufficiently high average degree of polymerization. The substance can also be made by hydrogenation of rubber, although it seems that this hydrogenation never removes all the double bonds, and is always accompanied by a substantial degradation of the chains. Nevertheless, Staudinger[53] obtained samples which were less elastic than rubber, which seems to agree with the position this material holds in Table III.

cis-POLYISOPRENE.—Rubber has an identity period of 8.1 Å.U., and, according to Bekkedahl and Wood[54], its melting point is 11° C; the heat of fusion is close to 4 calories per gram, or 270 calories per mole of isoprene (68 grams). In the unstretched state rubber shows an amorphous diagram[55], but crystallizes if stretched beyond 200 per cent[56]. Its crystal structure has been repeatedly investigated[57], most recently by Morss[58] and Bunn[51]. The cis configuration provides for a certain bulkiness of the chain, which makes it difficult to fit it into a lattice. Therefore the material has the tendency to contract, as soon as the external forces cease to straighten out and align the chains. Only one crystallographic modification of cis-polyisoprene is known at present. Experiments carried out by the writer to convert cis-polyisoprene into the trans isomer (rubber into gutta-percha) have been unsuccessful. On cautious heating of a rubber solution in a high-boiling solvent, cyclization always seems to occur at a higher rate than isomerization.

As far as present knowledge goes, it has not been possible to build up a pure cis polymer by synthesis. The pure trans polymer is not obtained either, but a copolymer with a certain excess of the trans configuration.

trans-POLYDIMETHYLBUTADIENE results from polymerization of dimethyl-butadiene; it has been called "methyl rubber", and gives an amorphous diagram in the unstretched state. On stretching, a fiber diagram of moderate quality is obtained, which allows the identity period to be estimated to about 5 Å.U. This, and the weakness of the diagram, point to the fact that the material is a cis-trans copolymer with a certain excess of pure trans chains. It has rubberlike properties, and seems to have a lower melting point than rubber. No figures, however, are available.

POLYISOBUTYLENE is obtained, according to Frolich and his coworkers[59], by polymerizing isobutylene at −75° C, with boron trifluoride as catalyst. It is amorphous but, on stretching, develops a distinct fiber diagram which was studied by Brill and Halle[60] and more recently by Fuller, Frosch, and Pape[61]. The fiber period is 18.63 Å.U., showing that such highly substituted chains do not fit easily into a lattice, and need a comparatively large number of monomers to restore geometrical identity. It is, therefore, to be expected that polyisobutylene will exhibit the properties of a typical rubber with low melting point (around or below 0° C) and strong tendency for the chains to contract. This appears to be fairly well supported by the experiment.

## COMPARATIVE CONCLUSIONS FROM TABLE III

If a pure trans-polybutadiene could be prepared, it would presumably head the list, because the forces between the double bonds are somewhat stronger than the ones between —$CH_2$—$CH_2$— groups. (Compare, for example, the melting and boiling points of ethylene and ethane or butadiene and butane. However, due to the presence of the double bonds in the chains, the free rotation about the adjacent single bonds is less hindered than in polyethylene.)

Bunn's discussion[51] of gutta-percha modifications shows that *trans*-configurated chains can be easily fitted into a lattice, and hence the gain in randomness on melting (entropy of fusion) is comparatively small.   If the (interpolated) heat of melting of *n*-butylene (around 310 calories per mole) is divided by the entropy of fusion of $\alpha$-gutta-percha[62] (0.82 calorie per gram$^{-1}$), a melting point of 380° K or 107° C is obtained.   This material would be a plastic rather than a rubber.   It may be that an excess of the *trans* modification is sometimes responsible for the limited extensibility of polybutadiene preparations, even when they are not cross-linked.   The actual products of the polymerization of butadiene is never the pure *trans* polymer, but a copolymer of *cis* and *trans;* this is listed as No. 7 and, as a result of prevented crystallizability, has more rubberlike properties than either the pure *trans* or the pure *cis* modification.

Polyethylene has been thoroughly investigated; the chains fit easily into the lattice, the gain in randomness on melting, $\Delta S = (\Delta H/T_m)$, is low and, hence, the melting point is high.   Taking the heat of melting of long-chain paraffins as 300 calories per mole and dividing by $T_m$ gives $\Delta S = 0.77$, which characterizes this material at normal temperatures as a plastic.

$\alpha$-Gutta-percha and $\beta$-gutta-percha have comparatively low degrees of polymerization, which must be pointed out before they are compared with the other polymers of Table III.   However, the degree of polymerization seems to be high enough to allow a cautious comparison.   (As Bunn remarked, rubber or Buna fractions of a polymerization degree of around 1000 behave like a rubber and not like a plastic.)   If one adopts this point of view, it can be understood why both materials behave like plastics at room temperature, and Bunn also showed how the differences in structure of the alpha and beta modifications may account for the different melting points.

*cis*-POLYBUTADIENE is not known, and hydrogenated rubber is presumably too degraded and, eventually, cyclized to be compared with the other substances.   Both materials should be at the transition point between plastics and rubbers.

*cis-trans*-COPOLYBUTADIENE has a typical tendency to contract and seems to start the materials with rubber properties.   Unfortunately, few qualitative data are available on this substance.

Rubber is the most thoroughly investigated of the polyhydrocarbons.   Its tendency to escape crystallization is represented by the comparatively high entropy of fusion and consequently low melting point.

Little is known about polydimethylbutadienes except that the accumulation of methyl groups makes the amorphous state comparatively bulky.   Their average degree of polymerization is low, and hence a straightforward comparison is not possible.   The copolymer displays the properties of a soft rubber.

Polyisobutylene is the material with the lowest tendency to crystallize, and from this point of view concludes Table III.   On fusion it gains 1.0 entropy unit per mole of monomer.

Table III is a scheme which can be improved.   However, even in this preliminary state, it shows that the polyhydrocarbons extend from highly rubberlike to typical plastic materials.   The melting points range from 0° to 120° C, and reflect the varying readiness of the chains to crystallize.   The more one prevents the fitting of the long molecules into a lattice, the higher is their tendency to return to the random state and the more pronounced are the rubberlike properties of the material.   If the entropy of fusion is below 0.85 entropy unit per mole of monomer, plasticlike substances appear; if it is above 0.95, typical rubbers are obtained.   In all cases in Table III, the heat

of fusion is of a similar order of magnitude, because the intermolecular forces are represented by (comparatively weak) homopolar van-der-Waals interaction.

However, it may be that, even if the specific molar cohesion is high (above 2000 calories as calculated in Table II), rubberlike properties can be obtained if steps are taken to prevent crystallization.

Polyvinyl alcohol in the water-swollen state and copolyvinyl chloride-acetate in the plasticized state seem to support this point of view.

If adopted as a working hypothesis, these results indicate that rubberlike properties can be obtained, not only with polyhydrocarbons, but with all types of straight flexible chain polymers, provided one succeeds in balancing the intermolecular forces by a sufficiently bulky construction of the chains so that the entropy of fusion has a value above 0.9.

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[62] *n*-Butylene is nearly identical with the monomeric unit of polybutadiene, and the entropy of fusion of α-gutta-percha should most closely represent the entropy of fusion of trans-polybutadiene.

# UNSATURATION OF SYNTHETIC RUBBERLIKE MATERIALS *

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The quantitative determination of rubber unsaturation has concerned numerous investigators. The use of iodine chloride as a reagent for this purpose (the well-known Wijs method) has achieved favor in recent years[1]. Under the proper experimental conditions, addition has been shown to be quantitative, and substitution reactions can be kept at a minimum[2]. This procedure has likewise been rather extensively employed as a measure of the residual unsaturation of various rubber derivatives[3].

This reagent does not, however, add quantitatively to all unsaturated compounds, regardless of structure[4]. The presence of a negative substituent on one or more of the unsaturated carbon atoms inhibits the reaction; in fact, it may entirely prevent it, as in the cases of maleic or fumaric acids or dichloroethylene[5]. In other compounds extensive substitution may occur along with addition, as in the case of the unsaturated terpenes[6].

The unsaturation of the polymerized diolefins should be of considerable interest, especially in comparison with natural rubber. It should be of special interest to study the comparative reactions with iodine chloride, which has become practically a standard reagent for rubber. Kemp and Mueller[4] mention that polychloroprene, to which they erroneously refer as polyvinyl chloride, adds iodine chloride to only 30 per cent of theory. This could be due to two causes—the negative influence of the chlorine attached to an unsaturated carbon, and/or possible cross-linkage between chains (cyclization). It is well established that polychloroprene is much less reactive chemically toward other reagents than is natural rubber[7]. It is unfortunate that Kemp and Mueller did not state with more detail the history of the sample studied, as such a result might have shown some interesting correlation with the experiments reported in this paper.

Thomas et al.[8] report that the unsaturation of the class of materials known as Butyl Rubber is between 1 and 2 per cent of that of natural rubber, as determined by iodine number. Presumably some modification of the Wijs method may have been employed, although no experimental details are given.

The polymers and copolymers of butadiene have been and are achieving industrial and military significance, both in this country and in Europe. It was therefore deemed of interest to study the chemical unsaturation of some of the other typical examples of this group of materials. Thornhill and Smith[9] reported the unsaturation of a typical commercial sample of this type. Since the exact composition was not known, the results are not indicative of much, other than the fact that some sort of value can be obtained by the general application of the standard method.

Rubberlike materials of the butadiene class have been shown by the work of Marvel[10] and others to possess a lower degree of linearity and regularity than those polymers produced by "polycondensation". Pummerer[11] studied

the ozonolysis cleavage products of sodium butadiene rubber, and failed to find succinic dialdehyde and succinic acid, which would be the products from a straight linear polymer of the 1,4 type. His work seems to indicate that there is a considerable amount of 1,2 polymerization, as well as 1,4, and that both may occur in the same unit, giving rise to cross-linkage or cyclization. This cyclization seems to occur spontaneously in storage with all the butadiene polymers, and stabilizers such as phenyl-$\beta$-naphthylamine are usually incorporated with the polymer to prevent this[12].

## EXPERIMENTAL PROCEDURE

Three polymers were employed: a sodium butadiene polymer and emulsion copolymers of butadiene-styrene and butadiene-acrylic nitrile, in which the weight ratios were 4 butadiene to 1 styrene and 7 butadiene to 3 acrylic nitrile, respectively[13]. The copolymers may be regarded as typical of the commercial American products, while the sodium polymer is an example of one type of European synthetic rubber.

The actual unsaturation of these materials is a function of several variables. For instance, there is as yet no adequate measure of the actual extent of cyclization occurring during polymerization or during storage. Other ingredients present during polymerization undoubtedly alter the extent of linear unsaturation in the polymer; in fact, some of them are often added for this purpose[14]. Further, there is definite proof that the two monomers do not always combine in exactly the proportions added, and that the ratio varies, at least under some conditions of polymerization, with the yield to which the reaction is taken[14]. The ratios assumed for purposes of calculation are those which are believed to represent the best approximation of the actual structure, as revealed by "materials balance"[15].

For purposes of calculation, the polymerization has been assumed to proceed in an orderly linear fashion. For the butadiene polymer, then, there would be one double bond per $C_4H_6$ unit, corresponding to an iodine number of 469.3. In the styrene copolymer, one-fifth of the weight should contribute no unsaturation, the remainder being $C_4H_6$ units. The iodine value is therefore four-fifths of the above, or 375.4. Likewise, the theoretical unsaturation of the acrylic nitrile copolymer is seven-tenths of 469.3, or 328.5.

The samples were sheeted on a mill, extracted 8 hours with alcohol to remove the inhibitor, dried, and stored in a vacuum desiccator until use. The sheeted sample was cut into small pieces before use. Under these conditions of storage the cyclizing effect did not seem to be rapid, but samples stored for periods longer than one month showed progressive diminution of iodine value. Wherever possible, determinations were made on the original master batch of purified sample, to prevent any possible variations due to differences in sample history.

Kemp has indicated some of the variables affecting the reaction, such as temperature, excess of reagent employed, time of reaction, and effect of solvent. In general, he found that shorter reactions at room temperature gave the same values as longer reaction at 0° C, but that after periods of the order of 20 hours, substitution began to be evident. The effect of solvent is also worth noting; in general, carbon disulfide seemed to be the most satisfactory.

The choice of solvent was dictated to some extent by the characteristics of the polymer under study. Some thirty solvents were investigated as potential media for the reaction; with a few exceptions they were not of much value.

Carbon disulfide seems to function fairly efficiently for the butadiene polymer and the styrene copolymer, but is valueless for the acrylonitrile copolymer. To compare the three polymers, a series of determinations was made in chloroform, which seems to be a fairly efficient solvent functioning across the entire series. None of these polymers were soluble to the same extent as rubber. Furthermore, it was preferred to avoid heating the solutions, since heat has been shown to exert a cyclizing effect on these polymers[16].

A 0.1-gram sample was allowed to swell in 50 cc. of solvent overnight, and then shaken to break up the swollen lumps. The solution and subsequent treatment were carried out in a 500-cc. wide-lipped assay flask, which was coated black to avoid any substituting effect of light upon the reaction. Twenty-five cc. of 0.2 $N$ iodine chloride, prepared according to Kemp, were then added. Although Kemp states that for rubber the solution should be clean and free of precipitate after the addition, this condition could not be realized in these samples, since the solubility of the polymer was definitely decreased by the addition of the acetic acid solution of the reagent; consequently the polymer precipitated in small particles throughout the solution. The glass stopper was moistened with 15 per cent potassium iodide solution and sealed with paraffin. This precaution was necessary to prevent loss of reagent. The flask was then placed in a constant-temperature bath for the requisite time.

Experiments at 0° C indicated that a satisfactory reaction could not be obtained in a reasonable time at this temperature. For this reason most of the reactions were run at 30° C. After removal of the flask from the bath, a portion of 25 cc. of freshly prepared potassium iodide solution was poured in the wide lip of the flask before the seal was broken. In this manner any liquid tending to escape was absorbed in the iodide solution and returned to the flask. The remainder of the potassium iodide solution and 50 cc. of freshly distilled water were added, and the solution was titrated immediately with 0.1 $N$ thiosulfate and starch. The polymer precipitated during the titration and tended to occlude iodine. It was therefore relatively easy to obtain transient end points. In general, an end point which persisted for 2 minutes was regarded as satisfactory. The results varied somewhat with the rate of titration, which was as rapid as possible.

The Blake and Bruce method of solution in $p$-dichlorobenzene[17], which is of special value for vulcanized rubber samples, was investigated and found to be of no value here. In fact, it has several distinct disadvantages for these polymers, such as tendency toward cyclization during the long heating necessary and precipitation of the polymer when the solution is dissolved in another solvent.

The analytical results are summarized in Table I. For comparison the iodine numbers are expressed in terms of the theoretical values for the specific polymers. In general, the most satisfactory behavior was obtained with the carbon disulfide solutions. The chief disadvantage of carbon disulfide as a solvent is its high vapor pressure at the temperature employed. Chloroform, although a better uniform solvent for the three polymers, gives solutions which show more tendency to form emulsions during titration. Although benzene gave the highest value and the nearest to theoretical in a comparative series, its solubility characteristics and general behavior are not entirely satisfactory, and it cannot be recommended.

Attempts to determine substitution in these reactions met with little success. The method employed was that of McIlhenny[18] as modified by Lewis

TABLE I

SUMMARY OF ANALYTICAL RESULTS AT 30° C

| Polymer | Solvent | Reaction time (hrs.) | Iodine No. | Percentage of theoretical |
|---------|---------|------|------|------|
| Butadiene | CS₂ | 2[a] | 336.4 | 71.8 |
| | CS₂ | 2 | 382.0 | 81.3 |
| | CS₂ | 4 | 386.9 | 82.4 |
| | CS₂ | 6 | 400.0 | 85.2 |
| | CS₂ | 22.5 | 420.9 | 89.6 |
| | CS₂ | 48 | 428.5 | 91.3 |
| | CS₂ | 168 | 436.7 | 93.1 |
| | CS₂ | 336 | 479.7 | 102.2 |
| | Chloroform | 2 | 348.2 | 74.1 |
| | Chloroform | 4 | 358.4 | 76.4 |
| | Chloroform | 22 | 405.2 | 86.2 |
| | Chloroform | 48 | 408.5 | 87.0 |
| | Chloroform | 168 | 408.7 | 87.1 |
| | Chloroform | 336 | 459.0 | 97.9 |
| | Benzene | 4 | 450.0 | 96.9 |
| | Xylene | 4 | 155.0 | 33.0 |
| Butadiene-styrene | CS₂ | 2 | 238.8 | 63.6 |
| | CS₂ | 4 | 288.3 | 77.0 |
| | CS₂ | 24 | 337.8 | 89.9 |
| | CS₂ | 48 | 337.8 | 89.9 |
| | CS₂ | 192 | 337.4 | 89.7 |
| | Chloroform | 2 | 204.1 | 54.3 |
| | Chloroform | 4 | 286.2 | 76.2 |
| | Chloroform | 22 | 334.1 | 88.8 |
| | Chloroform | 48 | 334.3 | 89.0 |
| | Chloroform | 168 | 310.6 | 82.6 |
| | Chloroform | 336 | 281.8 | 74.9 |
| Butadiene-acrylnitrile | Chloroform | 2 | 266.7 | 81.2 |
| | Chloroform | 4 | 268.0 | 81.4 |
| | Chloroform | 22 | 276.9 | 84.1 |
| | Chloroform | 48 | 286.0 | 87.0 |
| | Chloroform | 168 | 298.7 | 90.7 |
| | Chloroform | 336 | 271.1 | 82.4 |

[a] Experiment carried out at 0° C.

and McAdams[19]. Fugitive and nonreproducible end points were obtained in both carbon disulfide and chloroform. Some of the difficulty may have been due to hydrolysis of the iodochloride, as suggested by Kemp and Mueller[4]. Although substitution may have occurred during some of the reactions, there was no satisfactory measure of it. As far as natural rubber is concerned, Kemp and Mueller feel that the combination of a glacial acetic acid solution of iodine chloride and carbon disulfide as a solvent for the rubber exerts a powerful repressive influence on side reactions such as substitution and hydrolysis[20]. Furthermore, the relatively long flat portion of the curve is taken as additional evidence that little substitution had occurred; there is support for this assumption in the somewhat higher values obtained with very long reaction periods.

## DISCUSSION OF RESULTS

Several conclusions may be reached by a study of the data included in Table I and plotted in Figure 1. The reaction proceeds much more slowly

with all these polymers than with rubber. There is a fairly rapid initial reaction, followed by a rapid leveling of the curve in all cases which indicates that most of the addition has occurred. The increase in iodine value on prolonged reaction in the case of the butadiene polymer is undoubtedly the beginning of substitution. Since this requires nearly 2 weeks and since the curve is practically flat after 24 hours, we may assume that the addition reaction has reached equilibrium after 24 hours at 30° C. This compares with 15 minutes or less required for rubber. The styrene copolymer in carbon disulfide has likewise reached equilibrium in 24 hours. This marked difference in reactivity between these synthetic types and natural rubber agrees with their well-known resistance to aging and to the action of chemical reagents[21].
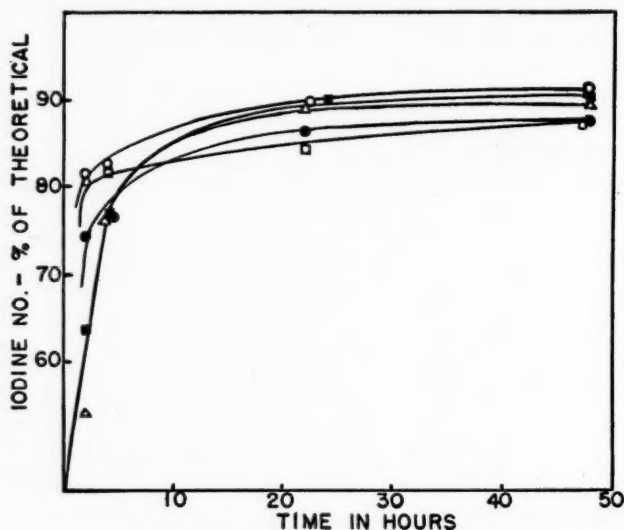


Fig. 1.—Iodine values of polymers vs. time.
O Butadiene polymer in carbon disulfide.
● Butadiene polymer in chloroform.
■ Butadiene-styrene polymer in carbon disulfide.
△ Butadiene-styrene polymer in chloroform.
□ Butadiene-acrylic nitrile polymer in chloroform.

The results in chloroform give definite indication of cyclization on long reaction for both the copolymers, but the polybutadiene seems to have undergone substitution. At shorter periods of time, the results in chloroform are slightly lower than those in carbon disulfide, the difference being most pronounced for the polybutadiene. The experimental error is decidedly larger when chloroform is employed, so that, on the whole, the results in the two solvents may be regarded as showing reasonably good agreement.

The acrylonitrile copolymer shows less consistency in its behavior. If the 24-hour value alone is considered, we might conclude that the presence of the negative nitrile group had repressed the reaction. However, this polymer shows the most rapid initial rate of reaction, followed by a steady but very slow rise to a maximum value after a reaction period of 168 hours. After this, the value again drops. It is believed that probably the values obtained in 2 to 4 hours actually give a truer picture of the addition reaction for this polymer than do the values obtained in longer periods of reaction.

The single result obtained in benzene can be regarded only as an indication of a possible direction of future investigation. It was obtained after most of the other work had been completed, and therefore a more extended study in this solvent was not made.

The difference between the experimentally determined unsaturation and the theoretical values may be regarded as due to cyclization or cross-linking. It is interesting to note the fairly narrow range in which these values fall. Accepting the results obtained in carbon disulfide as being somewhat more reliable, both the butadiene polymer and the styrene copolymer contain about 10 per cent of cross-linkage, with the acrylonitrile copolymer apparently being somewhat more highly cyclized.

## ACKNOWLEDGMENT

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# THEORY OF RUBBER ELASTICITY FOR DEVELOPMENT OF SYNTHETIC RUBBERS *

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Two cardinal problems exist in connection with the production of synthetic rubbers: (1) choice of the type of synthetics, necessary raw materials, and methods of production, and (2) evaluation of the products obtained. The most important and characteristic property of synthetics (and of natural rubbers) is their long-range reversible elasticity.

This property is the one which distinguishes rubber from wax, chewing gum, etc., and makes possible its widespread use for a variety of purposes. Especially does it make possible the construction of tires. This property is so characteristic that any material possessing it may be called a "rubber", regardless of chemical constitution. In spite of the many attempts directed toward an explanation of rubberlike elasticity, this problem (a problem in the chemical physics of solids) continued to be puzzling for many years. A theory of the typical rubber elasticity will obviously be of great help in the production, processing, and evaluation of desirable synthetics.

To mention a concrete problem of vital interest, Butyl rubber has poor rebound at room temperature, but is as lively as natural rubber at 100° C. It is obvious that, when more is learned about the mechanics of what makes rubber bounce, a more lively Butyl rubber at ordinary temperatures may be produced.

The statistical theory of rubber elasticity[2] explains in terms of molecular structure why rubber has a long-range reversible elasticity and why it exhibits an anomalous thermo-elastic behavior. The essence of the statistical theory is based on two concepts. First, rubber consists of giant long-chain molecules. Secondly, a quasi-free rotation is assumed to exist in a rubber molecule around each carbon-carbon bond. An important consequence of this quasi-free rotation is that the molecules are coiled up in the unstretched state.

The retractive force in stretched rubber is then due mainly to the tendency of the stretched chain molecules to change from the stretched, less probable form to the more probable coiled-up form. This is in accord with the second law of thermodynamics and is not caused by forces. The kinetic motion of the quasi-free rotating groups is the principal cause of contraction.

This semiquantitative theory explained the anomalous thermoelastic behavior of rubber. In particular, it predicted a direct proportionality between absolute temperature and stress at constant length, if the dependence of the internal energy on the length were separated out. However, no conclusions could be drawn from it as to the nature of a proper stress-strain curve. The reason for this restriction was the following. As a model for bulk rubber, this

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theory assumed a large number of rubber chain molecules, and avoided consideration of the interactions between the strings or chains. However, this interaction must be considered if the model is to possess a finite volume.

Obviously, strong forces must exist between molecules to prevent their slipping bodily past one another. On the other hand, the existence of these forces is in apparent contradiction to the postulate of the statistical theory that the molecules are free to coil up into a configuration of maximum entropy or greatest probability.

Recently, however, a quantitative theory was developed by James and Guth[3]. This new theory introduces a clear-cut three-dimensional model for bulk rubber, and it also resolves the dilemma between flexibility (free rotation) of the chain molecules and the steric forces binding them to a network. It yields a single analytical expression for the stress-strain curve which exhibits the characteristic S-shape of the typical rubber stress-strain curves. Also it predicts the occurrence of "a thermoelastic inversion point" or critical extension, below which rubber shows normal thermoelastic behavior, and above which it is "rubberlike".

Let us consider first a sample of unstretched rubber. What is its molecular structure? It is a random network of flexible chains stretched throughout the mass of the rubber (Figure 1). Each element of this network, *i.e.*, a giant
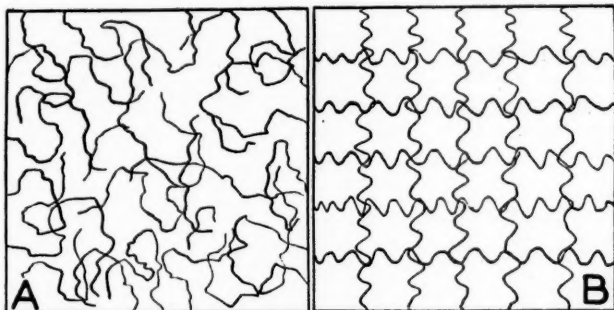


FIG. 1.—Cross-sectional representation of (A) random irregular network and (B) ordered network. In the theory it is proved that A may be replaced by B, in which the flexible chains run in the direction of three perpendicular coordinate axes.

long-chain molecule, tends to contract because of the intramolecular Brownian motion of these free-rotating rubber molecules. Just as a flexible string thrown up into the air will be more likely to come down in some curved form other than a straight line, a flexible rubber molecule will, in the unstretched state, be more likely to have a coiled rather than a straight form. This contracting tendency of the elements would lead to a collapse of the network, *i.e.*, to a more or less close-packed configuration. However, the tendency to close packing is counteracted by steric forces acting in the opposite direction in the chain molecule, *i.e.*, in the elements of the network and the joints between neighboring chain molecules. This second agent may be pictured as an outward push due to the outward pressure of a fictitious incompressible liquid through which the network of chain molecules extends. This simulates in effect the intermolecular forces which regulate the volume of the material.

For the unstretched state there must be an equilibrium between these two agents, *viz.*, the inward pull due to the contracting tendency of the network

and the outward push due to the pressure of the "liquid". This equilibrium condition serves to determine the pressure of the "liquid" if the contracting force is known. The contracting force may be derived by simple probability considerations of thermodynamics and has the form:

$$F = KTL \tag{1}$$

where $K$ = a constant which characterizes the rubber network; $T$ = absolute temperature; $L$ = relative length (that is, extended length divided by original length.

For a unilateral stress in the $x$ direction and for an incompressible material like rubber, a unit cube before stretching will be transformed into a parallelopiped of the same volume with the sides $L_x$, $L_y$, $L_z$. The equilibrium condition applied, for instance, to the free $y$-$z$ surface leads to the equation:

$$F = KTL_y = PL_xL_z \tag{2}$$

where $P$ is the internal pressure we wish to determine.

We have the conditions:

$$L_xL_yL_z = L_xL_y{}^2 = 1 \tag{3}$$

$$\text{hence } P = KT(1/L_x) \tag{4}$$

That is, the pressure decreases if the cube is extended and increases if it is compressed.

If, now, an external force is applied, the equilibrium condition will be that the inward-acting agents again should equalize the outward-acting agents. The external force represents an outward pull. Assuming that the stretch takes place in the $x$ direction, this equilibrium condition is obtained:

$$F + PL_xL_z = KTL_x \tag{5}$$

Using the values of $P$ and the incompressibility condition, we obtain as a final result the equation:

$$F = KT(L_x - 1/L_x{}^2) \tag{6}$$

The first term in the parentheses is due to the contracting force, whereas the second term is due to the pressure of the "liquid". This stress-strain curve has all characteristics of the rubber stress-strain curves up to 200–300 per cent extension.

It must be emphasized that the quantity $L$ which enters here is the ratio of the extended length of the sample (which is kept the same for all temperatures) and of the original length at room temperature. Hence Equation 6 is not exactly true if the temperature changes, and it is easy to see that the only change we have to make is to correct the internal pressure, replacing $1/L_x{}^2$ by $[1 + \alpha(T - T_0)]\,1/L_x{}^2$. Then the equation reads:

$$F = KT\left( L_x - \frac{1 + \alpha(T - T_0)}{L_x{}^2} \right) \tag{7}$$

Here the slope of the force will be zero if $L = 1 + (\alpha/3)(2T - T_0)$. A negative slope was discovered by Joule some eighty years ago and shows up both in natural and synthetic rubbers and in other rubberlike materials—for instance, in polystyrenexylene mixtures[4].

The theory shows that, for high extensions only, the contracting force changes its dependency on extension. The internal pressure remains prac-

tically the same. This change of the contracting forces leads to an upward turn of the stress-strain curve, and gives the characteristic S-shape of typical rubber stress-strain curves. We have proved that there are rubber compounds which show an S-shaped stress-strain curve in a range of extensions where no crystallization enters. This is the case for Buna types of synthetics particularly. Crystallization is sufficient to produce an S-shaped stress-strain curve, but it is not necessary for it.

Experiments on natural and synthetic rubber have revealed that the theory checks better with natural rubber than with synthetics, especially those containing carbon black. A correlation of the changes of the constants of the theory with those of the polymerization conditions should lead to the development of synthetics with more desirable properties. In addition, our theory permits a better evaluation and correlation of the thermoelastic properties of synthetics than the usual testing methods.

It appears to be better, when studying synthetics, to use a higher speed of stretching than the usual 20 inches per minute. At higher temperatures and higher extensions synthetics flow at a rate which depends on the speed of the stretching. The rate of flow differs for each particular compound. Therefore, fast stretching is necessary to eliminate the plastic flow.

A detailed discussion of this new theory will be published elsewhere.

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# EQUATION OF STATE OF SOME SYNTHETIC RUBBERS *

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The synthetic rubbers thus far developed bid fair to replace rubber permanently in hundreds of its varied uses. Though no one synthetic can, as yet, replace rubber in all of its applications, there are several synthetics available, each one of which excels rubber in one particular property. For example, some synthetics are oil- and gasoline-resistant, others resist the aging effects of heat, light, and oxygen, while still others surpass rubber in their resistance to flexing and abrasion.

On the other hand, there are no synthetics that can match the tensile strength, extensibility, and retractability of rubber at extreme temperatures. At low temperatures a stiffening and leathery behavior with large loss of elasticity is characteristic of most synthetics. At higher temperatures, plastic flow and permanent set are much more pronounced in synthetics than in rubber. Until these undesirable properties can be suppressed in synthetics, rubber will remain irreplaceable in many of its present uses.

To guide future development toward a better understanding of these problems, it is necessary to study the properties of the materials at hand and, from an analysis of the data, attempt to prescribe the course of further improvements. Such a program requires not only intensive experimental research, but also a theory of the phenomena being studied. In the case of rubber, the equation of state was developed from statistical theory[1] and was verified experimentally[2]. Since this theory was derived from a consideration of the general characteristics of long-chain or highly polymerized molecules, it is not confined to natural rubbers, but may be expected to apply also to synthetic polymers.

The purpose of this work was thus twofold. First it was desired to obtain experimentally the equations of state for several representative synthetic rubbers. Secondly, by comparing the results so obtained with the statistical theory of James and Guth, the applicability of the theory to synthetic rubber could be checked and its usefulness thereby extended.

## EXPERIMENTAL PROCEDURE

In general, the thermodynamic equation of state of a stretched material can be expressed in terms of the force of extension as a function of relative length and temperature, where the relative length is taken as the ratio of the stretched and unstretched lengths. The relaxation method of obtaining this relation was employed as follows.

The samples were held at constant extension in a constant-temperature water bath. The force necessary to maintain constant extension was measured by a platform balance, one arm of which was connected to the upper end of the sample. By raising or lowering the balances with respect to the fixed lower clamp, all desired extensions could be attained, and these extensions

were measured with a cathetometer.   The samples were allowed to relax at the highest temperature to be used in the experiment, and the decay of force in time was noted.   Gradually the rate of relaxation approached a nearly constant value which was small enough so that a state of virtual equilibrium existed.

After this nearly constant rate of decrease of stress (less than 50 grams per sq. cm. per hour) was reached, the stress-temperature data were recorded by lowering the temperature of the bath in steps of 10–15° C, and noting the value of the force necessary to maintain constant extension.   After the lowest temperature was reached (about 10° C.), the procedure was reversed by increasing the temperature to check for reversibility.   The value of 50 grams per sq. cm. per hour mentioned above for the final time rate of decrease of stress was found to be sufficiently small so that, during the time required for a complete stress-temperature run (about 45 minutes), the decrease in stress due to relaxation was not detectable, as evidenced by complete reversibility of the stress-temperature curve to within experimental accuracy.

This experiment was performed on three samples: Hycar-OR-H, Neoprene-1333N191A, and Neoprene-1333N192A.

A sample of the stress-temperature data is shown in Figure 1.   The circles represent the original data taken with decreasing temperatures, and the crosses represent the data observed with increasing temperatures.   The consistency of these points, taken over an interval of about 45 minutes, demonstrates the existence of the state of virtual equilibrium.   The general characteristics of these curves, the straight lines, the negative slopes at low relative lengths, and the increasing slopes at higher elongations, are all in agreement with the data obtained for rubber.

The highest temperature indicated for Hycar is 50° C.   Both Neoprene samples, however, were tested up to 65° C.   The relatively low maximum temperature for Hycar was adopted because preliminary tests showed that this sample broke at higher temperatures, even though the extensions were very low.   At the lower temperature the range of relative lengths was greatly increased.

From these families of stress-temperature curves, a cross plot of stress-relative length curves at a constant temperature can be obtained.   Figure 2 shows a stress-relative length curve for two different temperatures.   The crosssing of these curves at a low relative length is consistent with the inversion of the slopes of the stress-temperature curves.   The inversion of slopes of the stress-temperature curves has been attributed to thermal expansion in the past, and in the case of rubber definite proof has been given[2].

In an attempt to explain this behavior, the following considerations are presented.   When an unloaded strip is subjected to an increase in temperature, the length of the sample is increased according to the ordinary expression for thermal expansion:

$$L = L_0 \left( 1 + \frac{\alpha}{3} \Delta T \right)$$

where $\alpha$ = volume coefficient of thermal expansion.

The physical model[1] of a network of stretched long-chain molecules predicts that an increase of temperature causes the molecules to tend to a more disordered or curled-up state.   Therefore, if a sample is extended to a certain critical relative length and the temperature is raised, the thermal expansion increases the original unstretched length, thereby decreasing the relative
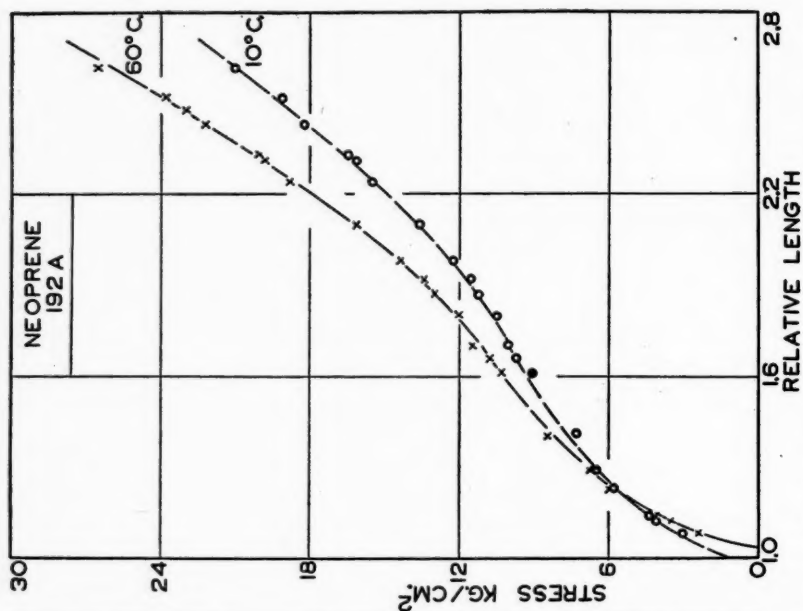
Fig. 2.—Stress-relative length curve at two temperatures.
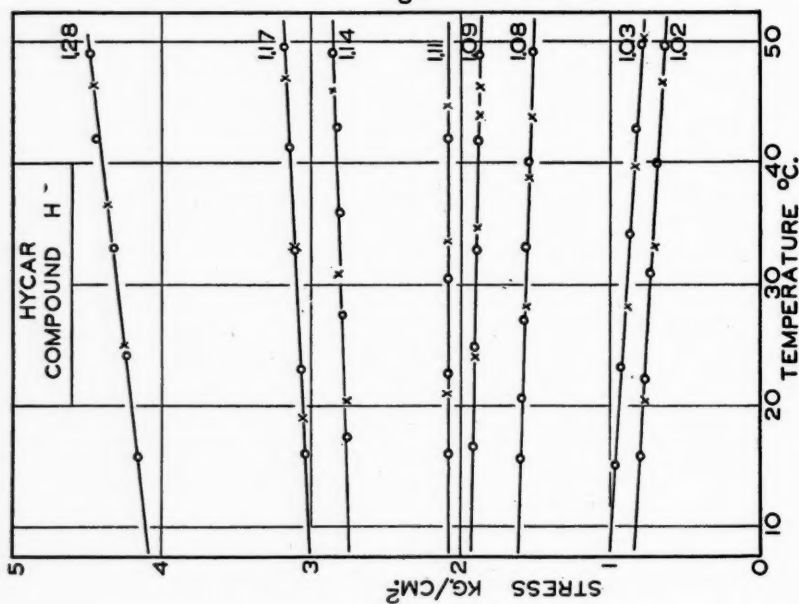


Fig. 1.—Sample of stress-temperature data.

length. This decrease in relative length requires less force to maintain the constant extension. But the increased retractive force due to the tendency of the molecules to curl up results in an increase in force necessary to maintain constant extension. At the critical elongation referred to above, these two opposite changes in force exactly counterbalance each other, and the net result is no change in force required to maintain constant extension. This critical elongation is referred to as the inversion point.

## DISCUSSION OF RESULTS

The stress-temperature curves obtained for the synthetics can be expressed in the form:

$$F = A(L) + B(L) \cdot T \tag{1}$$

where $A$ and $B$ are functions of relative length only. This is the equation of state of the materials studied, and is to be compared with the general equation of state derived from thermodynamics for a stretched material:

$$F = (\partial U/\partial L)_T - (\partial S/\partial L)_T \cdot T \tag{2}$$

where $U$ = internal energy
$S$ = entropy

Comparison of these two equations indicates that $A(L)$, which is the intercept of the stress-temperature curves on the $T = 0$ axis, is a measure of that part of the total force due to the change in internal energy accompanying the extension of the materials studied; the term, $B(L) \cdot T$, which is the product of the slope of the curves and the temperature, is a measure of that part of the total force which is due to entropy changes involved in the same extension. The identification becomes clearer if Equation 2 is written in the form:

$$F = \left(\frac{\partial U}{\partial L}\right)_T + \left(\frac{\partial F}{\partial T}\right)_L \cdot T \tag{3}$$

Here the entropy term is clearly the product of the slope of the stress-temperature curves and the temperature.

The resolution of the total stress into its two components can be done analytically, and Figure 3 shows graphically the results of such an analysis. The greater part of the total stress is accounted for by the entropy contribution, and the characteristic S-shape of the stress-relative length curve results from the entropy term.

The theory of Guth and James[1], which is derived from statistical considerations, should agree with the entropy contribution here. Although the extended theory is valid over a large range of relative lengths, it reduces to a simple form for small $L$. This approximate form of the extended theory at small elongations is:

$$F = KT\left[L - \frac{1 + \alpha(T - T_0)}{L^2}\right] \tag{4}$$

where $F$ = total stress
$K$ = a constant
$L$ = relative length
$\alpha$ = coefficient of expansion
$T_0$ = room temperature
$T$ = temperature at which $F$ is measured
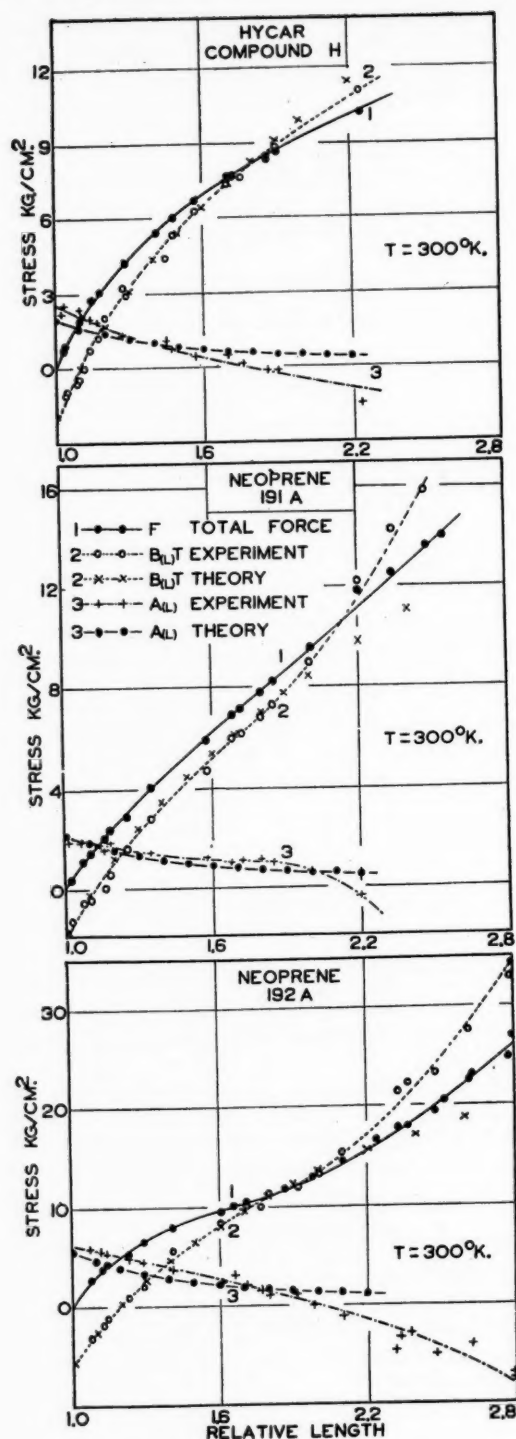
Fig. 3.—Resolution of total stress with two components.

The two components may be derived from Equation 4.    The entropy contribution is:

$$T\left(\frac{\partial F}{\partial T}\right)_L = KT\left[L - \frac{1 + \alpha(2T - T_0)}{L^2}\right] \tag{5}$$

$$\left(\frac{\partial U}{\partial L}\right)_T = K\alpha T^2/L^2 \tag{6}$$

To compare theory to experiment, constant $K$ must be evaluated.    Since, however, no values for $\alpha$, the thermal coefficient of volume expansion, were available, it was determined also from theory.    If $T(\partial F/\partial T)_L$ is plotted as a
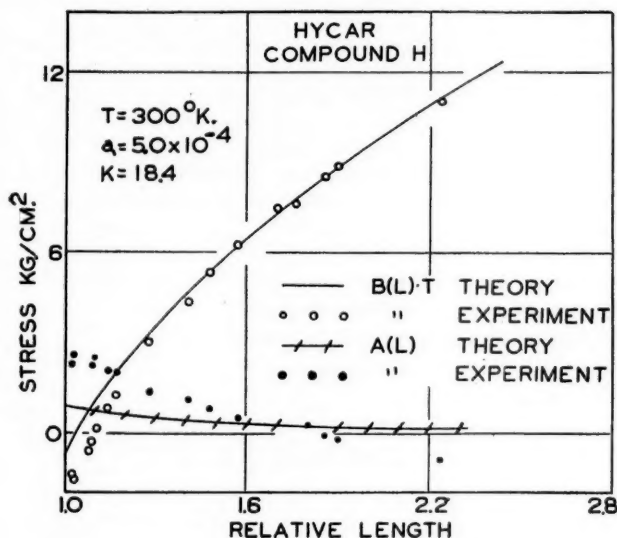


Fig. 4.—Modified comparison between experiment and theory.

function of relative length, the relative length at which this quantity is equal to zero can be determined.    From Equation 5, if $T(\partial F/\partial T)_L = 0$, then:

$$L^3 = 1 + \alpha(2T - T_0) \tag{7}$$

At the chosen temperature, $T = T_0 = 300°$ K., Equation 7 reduces to:

$$\alpha = (L^3 - 1)/300 \tag{8}$$

From Equation 8, $\alpha$ was determined for the three samples.    With the values determined for $\alpha$, constant $K$ can be evaluated by comparing Equation 5 to the entropy portion on Figure 3.    The values thus obtained are:

| Sample | $\alpha$ (° C.)$^{-1} \times 10^4$ | $K$ Kg./sq. cm./° K. |
|---|---|---|
| Hycar-OR-H | 11 | 19.75 |
| Neoprene-1333N191A | 14 | 17.0 |
| Neoprene-1333N192A | 22 | 28.0 |

Using these values for $\alpha$ and $K$ in the equations, the theoretical and experimental components can be compared.    As the graphs indicate, agreement for

the entropy contributions is good.   Since the theory is developed only from entropy considerations, the internal energy contribution, $(\partial U/\partial L)_T = K\alpha T^2/L^2$, cannot be expected to account for all the observed internal energy contribution.   However, the data on Figure 3 show surprisingly good agreement between experiment and theory for Hycar and both Neoprene samples.

To obtain a more valid comparison, the volume coefficient of thermal expansion was recently measured by means of a mercury dilatometer[3].   The values for $\alpha$ differ from those predicted by theory by as much as one-half a magnitude.   With these values and the corresponding values for $K$, Figure 4 shows the modified comparison between experiment and theory.

## CONCLUSIONS

Although the three synthetic samples exhibit plastic flow and permanent set to a greater degree than rubber, they are truly rubberlike in physical properties.   All three types display the same general features of stress-temperature behavior.   The stress-relative length curves have the same shape. The same equation of state that characterizes the behavior of rubber also describes, in terms of relative length and temperature, the retractive force exerted by these samples when stretched.   As far as we know, this equation of state for Hycar and two Neoprene compounds is the first to appear in the literature for any synthetic rubber.

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# EQUATIONS OF STATE FOR NATURAL AND SYNTHETIC RUBBER–LIKE MATERIALS. I

## UNACCELERATED NATURAL SOFT RUBBER *

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### INTRODUCTION

The most important and the most characteristic property of rubber is its long-range reversible elasticity. This unusual property is the one which distinguishes rubber from wax, chewing gum, etc., and makes possible its widespread use for a variety of special purposes. This property is so characteristic that any material possessing it may be called a "rubber" regardless of its chemical constitution. In spite of many attempts to explain rubber-like elasticity, this problem—a problem in the chemical physics of solids—continued to be a very puzzling one for many years.

However, the statistical theory of rubber elasticity of Guth[1] made it possible to understand, in terms of molecular structure, why rubber has a long-range reversible elasticity, and why it exhibits an anomalous thermoelastic behavior. The essence of the statistical theory is based on two concepts: (1) rubber consists of giant long-chain molecules, and (2) a quasi-free rotation exists in a rubber molecule around each C—C bond. An important consequence of this quasi-free rotation is that the molecules are coiled up in the unstretched state.

The retractive force in stretched rubber is then due mainly to the tendency of the stretched chain molecules to change from the stretched, less probable form to the more probable coiled-up form. This is in accordance with the second law of thermodynamics, and is not caused by forces. The kinetic motion of the quasi-freely rotating groups is the principal cause of the contraction.

This semiquantitative theory explained the anomalous thermoelastic behavior of rubber. In particular, it predicted a direct proportionality between the absolute temperature and the stress at constant length, if the dependence of the internal energy on the length were separated out. However, no conclusions could be drawn from it as to the nature of a proper stress-strain curve. The reason for this restriction was that, as a model for bulk rubber, this theory assumed a large number of rubber chain molecules, and avoided consideration of the interactions between the strings or chains. However, this interaction must be considered if the model is to possess a finite volume.

Obviously, strong forces must exist between the molecules to prevent their slipping bodily past each other. On the other hand, the existence of these forces is in apparent contradiction to the postulate of the statistical theory that the molecules are free to coil up into a configuration of maximum entropy or greatest probability.

Recently, however, a quantitative theory was developed by James and Guth[2]. This new theory introduces a clear-cut three-dimensional model for

bulk rubber, and it also resolves the dilemma between flexibility (free rotation) of the chain molecules and the steric forces which bind them to a network.

It yields a single analytic expression for the stress-strain curve which exhibits the characteristic S-shape of the typical rubber stress-strain curves. It also predicts the occurrence of a "thermoelastic inversion point" or critical extension below which rubber shows normal thermoelastic behavior, and above which it is "rubberlike".

The main objective of this investigation was to obtain experimentally the equation of state for rubber. Just as the thermal properties of a gas are known if its equation of state can be found experimentally or derived theoretically, the thermoelastic properties of stressed rubber can be obtained from its equation of state. It is well known that the pressure exerted by a real gas held at constant volume can be expressed as the sum of two components, $viz.$, $P_u$, the contribution of the internal energy due to the intermolecular forces, and $P_s$, the contribution of the entropy due to the motion of the gas molecules:

$$P(V, T) = P_u(V, T) + P_s(V, T) \tag{1}$$

For a gas obeying van der Waals' law:

$$P = -\frac{a}{V^2} + \frac{R}{(V - b)} \cdot T \tag{2}$$

Here $P_u = -a/V^2$ and $P_s = RT/(V - b)$. Generally, for a gas $P_u$ is small compared to $P_s$ and for an ideal gas $P_u = 0$. However, only on the basis of kinetic theory may one say that the pressure of a gas under ordinary conditions is due principally to the motion of the gas molecules, whereas the contribution of the intermolecular forces is a second-order effect.

This comparison with the equation of state of a gas permits us to state our objective more precisely. We want to obtain the force $F$ acting on stressed rubber as a function of relative length $L$ (or per cent elongation) and absolute temperature $T$·

$$F = F(L, T) \tag{3}$$

By applying thermodynamics we can separate this force into the two components $F_u$, due to the internal energy, and $F_s$, due to the entropy. Experimentally we can measure the total force and the component $F_s$. We can also determine $F_u$, the amount of the contribution of the intermolecular forces. Thermodynamics alone is not adequate to give a kinetic interpretation of either $F_u$ or $F_s$. Moreover, in general, both $F_u$ and $F_s$ are made up of factors due to both kinetic motion and potential energy. Only by setting up a model for rubber, treating this model by statistical mechanics, and finally comparing separately experimental and theoretical $F_u$'s and $F_s$'s, are we in a position to offer a kinetic interpretation of either $F_u$ or $F_s$. Thus we are able to determine if the retractive force in stressed rubber is caused mainly by the motion of the rubber molecules, as predicted by the statistical theory of rubber elasticity developed by James and Guth[3].

## METHODS OF OBTAINING EQUATIONS OF STATE

In conformity with the three possible forms of the equation of state for stressed rubber, we have the choice of three types of measurement: (1) A family of isothermals, stress-strain curves, taken at different temperatures; (2) a family of isotonics, strain-temperature curves, taken at different stresses,

and (3) a family of isometrics, stress-temperature curves, taken at different strains.   Each of these three families of curves yields a complete determination of the stress as a function of length and temperature:

$$F = F(L, T)$$

In the foregoing, the existence of a unique relation: $F = F(L, T)$, was assumed. This is permissible if thermal hysteresis, aftereffects, etc., are eliminated experimentally.

The simplest method of investigating the equation of state experimentally might seem to be the direct determination of the family of isothermal stress-strain curves.   However, as is well known from the work of many investigators in this field, this procedure fails to yield a unique set of values of stress vs. strain.   In particular, the results obtained depend greatly on the speeds with which the curves are taken, as is evident, for example, by the work of Williams and Sturgis[4], Dart and Guth[5], and Roth and Holt[6].

To obtain significant results, it is necessary to employ a method which yields equilibrium curves, that is, stress-strain or stress-temperature curves which do not show hysteresis.   Prominent among the techniques used for this purpose in the past are those of Gerke[7], Holt[8], and Wiegand and Snyder[9], the method of repeated stretching employed by Williams and Sturgis[4], and the method of relaxation used by Meyer and Ferri[10] and by Guth and his collaborators Hauk and Neumann.   The older experimental results were discussed recently in this journal by James and Guth[3] from the point of view of the theory developed by these authors.   This discussion brought out the necessity of more complete and more accurate experiments along this line.

Because of the practical difficulties, already noted, which are encountered in attempts to obtain equilibrium stress-strain curves, all of the investigations mentioned above are limited in both accuracy and range of variables covered. These inadequacies will be brought out in more detail in the discussion of our results.   They were, however, the chief reason why a systematic experimental study of the equations of state of rubberlike materials was started by the authors, in order that experimental data might be obtained under conditions of observation corresponding to those assumed in the theory of James and Guth[2].

### EXPERIMENTAL PROCEDURE

After some preliminary investigations, the method of stress-relaxation, yielding isometrics, was selected as being the most suitable for this work. Dumbbell-shaped strips were used, and the elongation was determined by measuring the distance between two lines on the central portion of the strip with the aid of a cathetometer.   The composition of the samples was eight parts of sulfur per one hundred parts of pale crepe, vulcanized at 147° C for 180 minutes.   This particular composition was selected for three reasons: First, it was known to exhibit a small hysteresis effect and have small permanent set.   Second, from x-ray studies it is known that appreciable crystallization does not set in below 350 per cent.   Third, owing to the small number of ingredients (only rubber and sulfur) the general structure was not unduly complicated, and results should therefore be readily adaptable to comparisons with theory.   It should be noted also that, even if the high rate of aging makes this compound unsuitable for practical use, the aging presented no serious problem in this work.   The samples were immersed in a water bath, the lower end of the strip being mounted in a fixed clamp, and the upper end being held

by a clamp attached to one arm of a platform balance. The balance served not only to maintain the length constant, but also to measure the force and its variation with time.

The samples were permitted to relax at the highest temperature to be used in the experimental work until the time rate of decrease of stress was small and approximately constant. The temperature was then decreased in steps and the corresponding force values noted. To check reversibility, the temperature was then increased in steps to see if the original stress-temperature curve was followed.

The equilibrium point, or rather equilibrium range, on the stress-relaxation curves at which the stress-temperature data were taken may be described more exactly as follows: If we have not allowed sufficient time for the attainment of this region, branching will occur in the stress-temperature curves. That is, if we first decrease the temperature and then increase it again, we shall obtain two branches for our stress-temperature curves which meet at the lowest temperature, the upper branch corresponding to decreasing temperature, and the lower branch corresponding to increasing temperature. In this region of the relaxation curve, the sample exhibits semipermanent set and also appreciable stress relaxation. Relaxation times exceeding this value by appreciable amounts lead to permanent set, which increases in magnitude with time. Briefly then, this equilibrium point or range represents a region where semipermanent and permanent sets have their minimum values.

The proof that the above process leads to equilibrium in the sense of thermodynamics rests on the following arguments: (1) reversibility of the stress-temperature curves; (2) good agreement between experiment and the theory, which assumes that equilibrium conditions do exist; and (3) checking of the thermodynamic formulas which relate the three thermoelastic effects.

Checking of the thermodynamic formulas was not done in the present experiments. It is hoped that this may be done at a later date. However, Ornstein, Eymers, and Wouda[11] have checked the existence of equilibrium in the sense of thermodynamics on another (accelerated) pure-gum compound.

Although we do not wish to enter into a discussion of the physical nature of relaxation and creep phenomena in this paper, it seems interesting to point out how in two cases these phenomena have affected some of the older experimental work. (1) The hysteresis loops appearing in stress-strain curves, provided we are below the region of crystallization, are due to the phenomenon of relaxation. (2) The occurrence of these hysteresis loops, which indicates that equilibrium conditions have not been reached, explains why some older investigators have reported temperature effects on stress-strain curves in direct contradiction to those reported here.

## RESULTS AND THEIR THERMODYNAMICAL EVALUATION

Figures 1 and 2 show the stress-temperature curves so obtained for elongations ranging from 3 to 370 per cent. Readings taken at increasing temperatures to check reversibility are shown on the curves by crosses. It is seen that they are in good agreement with the curves obtained for decreasing temperatures, indicating that relaxation during the time needed for the stress-temperature run had been reduced to a negligible amount, and that there is no thermal hysteresis. In all cases the curves appear to be straight lines, and it is seen that their slopes increase with increasing elongations. For elongations less than 10 per cent, the slopes are negative. The elongations were
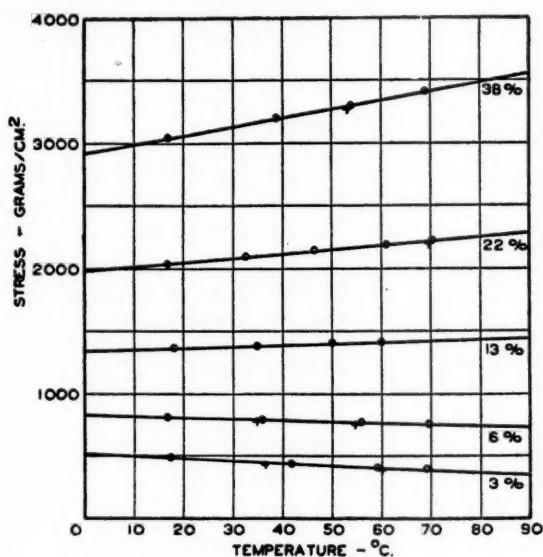
Fig. 1.—Stress-temperature curves obtained for elongations ranging from 3 per cent to 370 per cent.
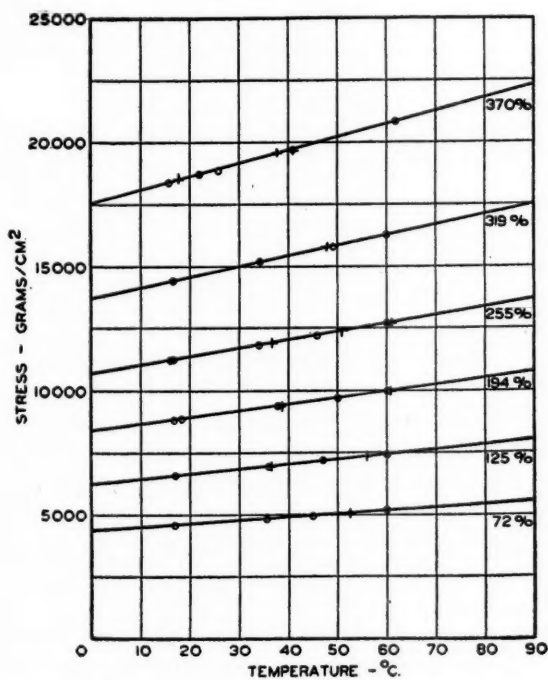


Fig. 2.—Stress-temperature curves obtained for elongations ranging from 3 per cent to 370 per cent.

computed for these curves on the basis of the unstressed length measured at room temperature after the run. Figure 3 shows the isothermal stress-strain curves obtained at 20° and 70° C from the stress-temperature curves of Figure 1. Note the crossing of the two curves at about 10 per cent elongation, as required by the inversion of the slopes of the stress-temperature curves at this point.
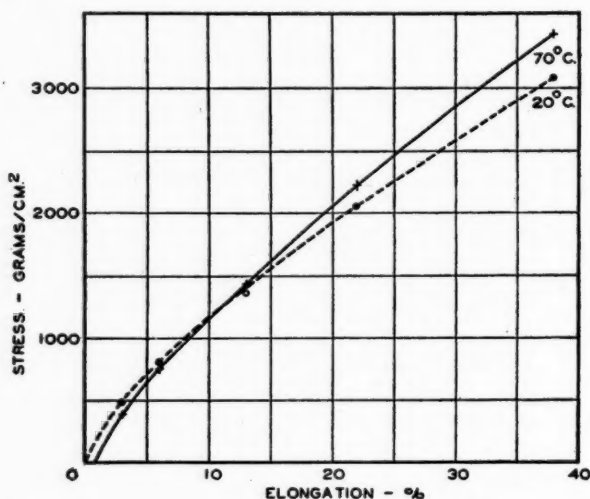


Fig. 3.—Isothermal stress-strain curves obtained at 20° C and 70° C from the stress-temperature curves of Figure 1.

The curves of Figures 1 and 2 represent the equation of state for our rubber. Since these curves are straight lines they may be expressed by the equation:

$$F = A(L) + B(L)T \tag{4}$$

where $F$ is the stress, $L$ the relative length, and $T$ the absolute temperature. The physical significance of $A(L)$ and $B(L)$ may be seen by comparing Equation (4) with the general thermodynamic relation:

$$F = \left(\frac{\partial U}{\partial L}\right)_T - \left(\frac{\partial S}{\partial L}\right)_T \cdot T = \left(\frac{\partial U}{\partial L}\right)_T + \left(\frac{\partial F}{\partial T}\right)_L \cdot T \tag{5}$$

where $U$ is the internal energy, $S$ the entropy, and the other symbols are as defined above. The term $\left(\frac{\partial U}{\partial L}\right)_T$ represents the contribution to the total stress due to the internal energy, while the term:

$$-\left(\frac{\partial S}{\partial L}\right)_T \cdot T = \left(\frac{\partial F}{\partial T}\right)_L \cdot T$$

represents the portion of the stress arising from the entropy contribution. In the following, for simplicity, we shall refer to the first of these terms as $A(L)$ and to the second as $B(L) \cdot T$. It is interesting to compare Equation (4)

above with van der Waals' equation of a real gas:

$$P = -\frac{a}{V^2} + \left(\frac{R}{V-b}\right) T$$

Now we know that, for a real gas, the pressure increases linearly with temperature. The similarity of Equations (4) and (2) indicates that the same behavior should follow for rubber. This is the case in Figures 1 and 2 for extensions above approximately 10 per cent, but is not true for the lower extensions. A question now arises as to why rubber should fail to follow this gaslike behavior at lower extensions. The negative slopes at small extensions and the existence of an inversion point are due to the volume thermal expansion which is present in both the stretched and the unstretched states of rubber. In particular, the rubber samples were held at constant length, but it does not follow from this that they were held at constant elongation, for at each temperature the unstressed length will have a different value, owing to ordinary volume expansion. The statistical theory also predicts this inversion if thermal expansion is taken into account. It is easy to calculate a corrected elongation on the basis of the unstressed length at the temperature in question rather than at room temperature.

To make this correction graphically, the following procedure was adopted. A set of stress-strain values was obtained at constant temperature from the curves of Figures 1 and 2. Each value of strain was corrected for volume thermal expansion by means of the equation:

Corrected percentage elongation

$$= \frac{\text{uncorrected percentage elongation} - 100\alpha\Delta T}{1 + \alpha\Delta T} \quad (6)$$

where $\alpha$ is the linear temperature coefficient of unstrained rubber having the composition described above, and $\Delta T$ is the temperature rise in degrees Centigrade above room temperature (25° C). The value of the expansion coefficient was taken from the data given by Scott[12]. This procedure was repeated for a number of different temperatures, viz., 10°, 30°, 50°, and 70° C, and a corrected set of isothermal stress-strain curves was drawn from these values. These are shown in Figures 4 and 5. It is seen that the curves no longer cross in the region of 10 per cent. From the curves of Figures 4 and 5, a new set of stress-temperature curves was plotted. These are shown in Figures 6 and 7, each line now representing a corrected elongation. It is seen that the slopes of all stress-temperature curves are positive even for elongations as low as 1 per cent, and that the rubber now follows the gaslike behavior at all extensions.

### RELATION OF THE RESULTS TO OTHER THERMOELASTIC EFFECTS OBSERVED FOR RUBBER

It is interesting to note that, although several investigators in the past have attributed this inversion point to ordinary volume expansion, it has never before this time, to the authors' knowledge, been quantitatively proved to be due to this cause. It should be emphasized also that the inversion point obtained when rubber is kept under constant load and the temperature is increased, as well as the inversion point in the heat developed when rubber is stretched quickly (first noted by Joule[13], occur at approximately the same
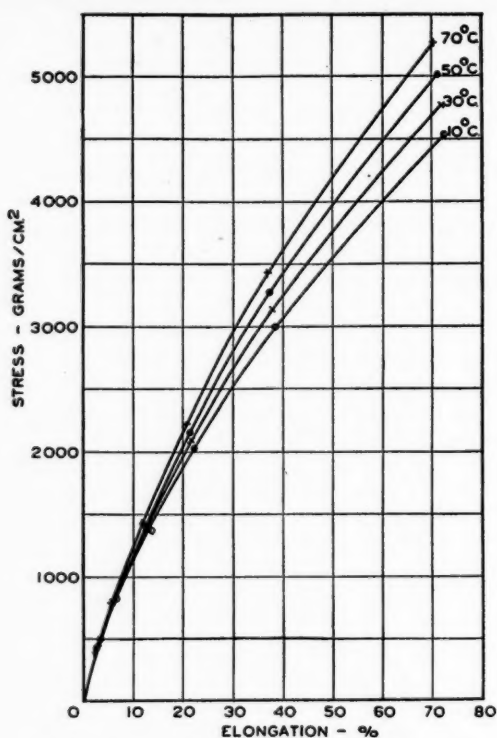
FIG. 4.—Corrected set of isothermal stress-strain curves.
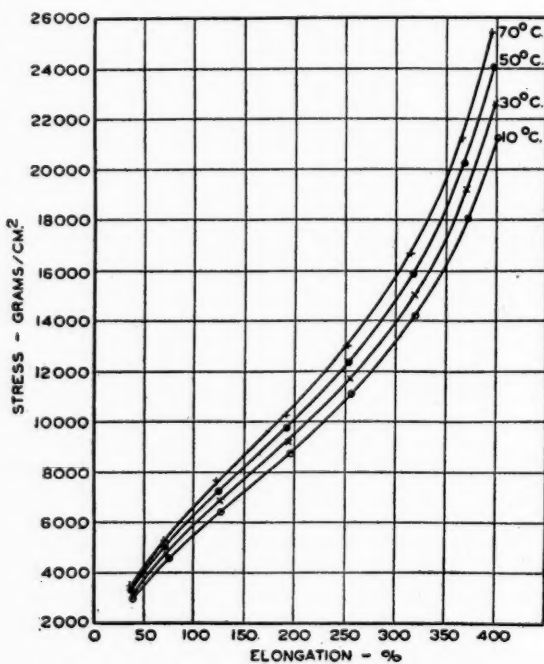


FIG. 5.—Corrected set of isothermal stress-strain curves.
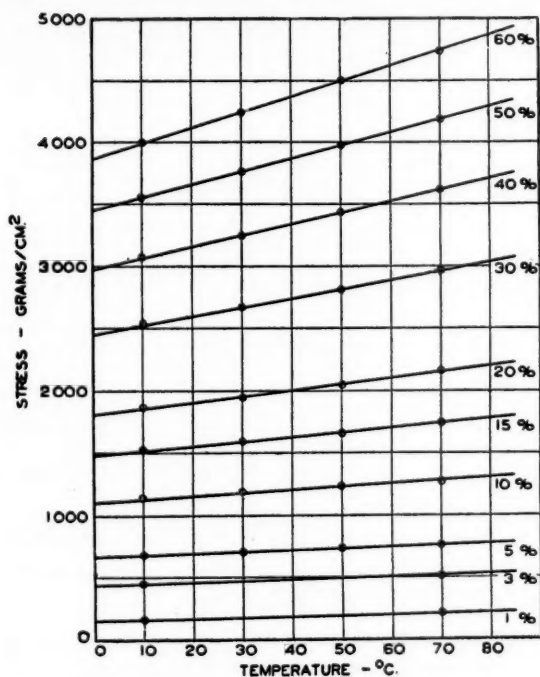
FIG. 6.—Corrected set of stress-temperature curves obtained from Figures 4 and 5.
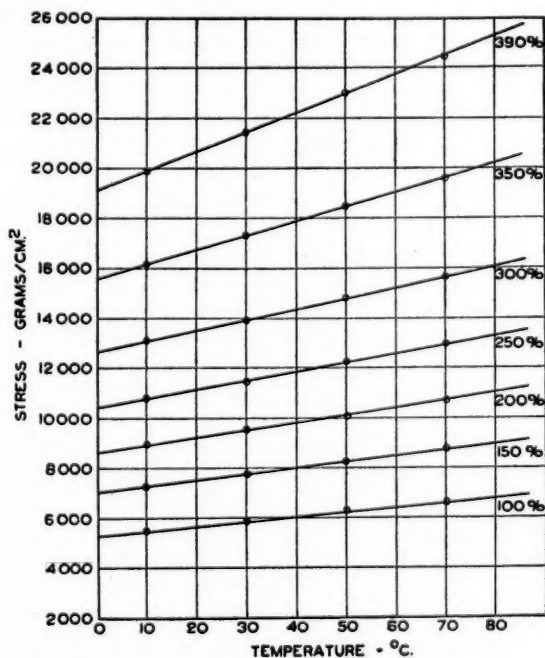


FIG. 7.—Corrected set of stress-temperature curves obtained from Figures 4 and 5.

extension, and may be explained in the same manner. For, according to thermodynamics, the inversion points for all three effects occur where the temperature coefficient of force changes its sign. For the isotonics, $L = L(F, T)$, we can derive the relation:

$$\left(\frac{\partial L}{\partial T}\right)_F = -\left(\frac{\partial L}{\partial F}\right)_T \cdot \left(\frac{\partial F}{\partial T}\right)_L \tag{7}$$

which, of course, changes sign when $\left(\dfrac{\partial F}{\partial T}\right)_L$ changes sign. For the heat generated on adiabatic stretching, Lord Kelvin[14] in 1855 derived the relation:

$$\Delta T = T \int_L^{L+DL} \frac{\left(\dfrac{\partial F}{\partial T}\right)_L}{C_L} \cdot dL \tag{8}$$

where $C_L$ is the specific heat at constant length. We see that $\Delta T$ is positive (increase in temperature) when $\left(\dfrac{\partial F}{\partial T}\right)_L$ is positive, and is negative (decrease in temperature) when $\left(\dfrac{\partial F}{\partial T}\right)_L$ is negative. Joule[13] found that $\Delta T$ is negative for extensions below 10 per cent and positive for extensions of about 10 per cent, in agreement with this experiment.

### DECOMPOSITION OF THE STRESS INTO ITS ENTROPY AND INTERNAL–ENERGY COMPONENTS

Interpreting Equation (4) in terms of the stress-temperature curves of Figures 6 and 7, we see that the term $A(L)$ is given by the intercepts of the straight lines on the absolute zero temperature axis and that the term $B(L) \cdot T$ is obtained from the product of the slopes of the straight lines and the absolute temperature. In Figure 8a the value of each term and their sum are plotted against the corrected elongations at 20° C. Figure 8b shows the same values plotted against the uncorrected elongations. In each case the sum represents the isothermal stress-strain curve.

It should be noted in Figure 8a that the term $A(L)$ contributes, in general, less than 10 per cent of the total stress, while the term $B(L) \cdot T$ exhibits all of the characteristics which one expects for a rubber stress-strain curve. We wish to point out that the separation of the stress-strain curve into its additive terms may be carried out, even if the stress-temperature curves were not straight lines. For, according to the general thermodynamic equation of state:

$$F = \left(\frac{\partial U}{\partial L}\right)_T + T\left(\frac{\partial F}{\partial T}\right)_L \tag{5}$$

the contribution of the internal energy is always given by the intercept of the tangent to the stress-temperature curves at the temperature desired.

In Figure 9 the quantity $B(L) \cdot T$, from Figure 8a, is plotted in arbitrary units against the elongation, and this curve is compared with the expression for the stress given by the statistical theory developed by James and Guth[2]. This theory neglects the internal energy not associated with thermal expansion, and assumes that the stress in stretched rubber (apart from that due to thermal expansion) is due to the tendency of a network of rubber molecules to return to a less ordered state or a state of higher entropy.
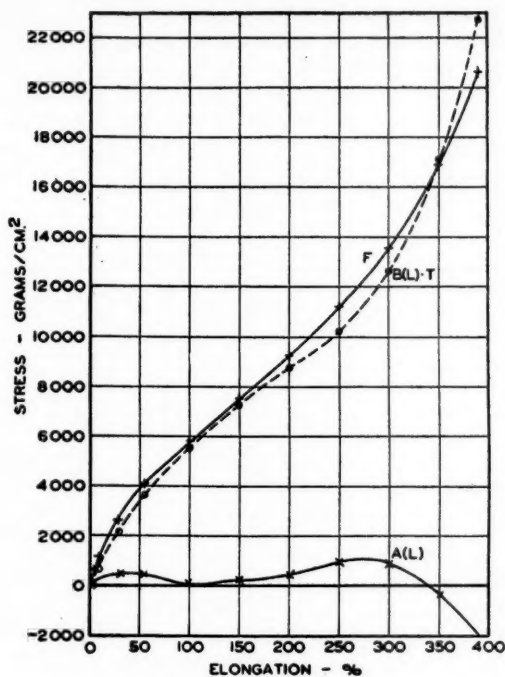
FIG. 8a.—Plot of the value of each term and their sum against the corrected elongations at 20° C.
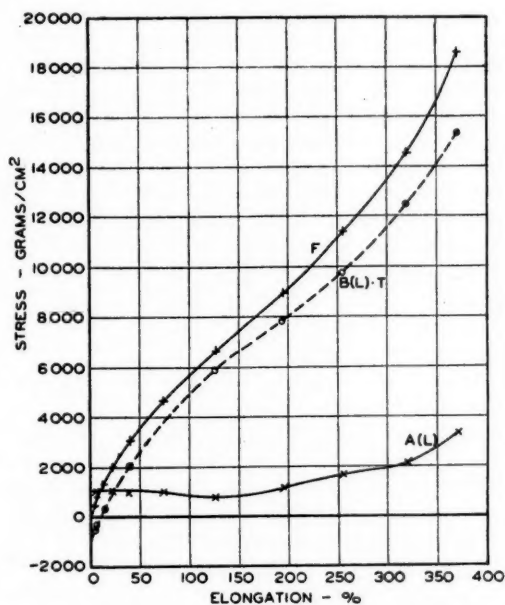


FIG. 8b.—Plot of the value of each term and their sum against the uncorrected elongations at 20° C.

The agreement is seen to be rather good up to an elongation of about 320 per cent. Above this point the two curves diverge, probably owing to the onset of crystallization, a factor not included in the theory. In connection with this it is interesting to note that the theoretical expression which neglects crystallization yields an S-shaped curve; hence, the S-shape is not necessarily due to crystallization. From the experimental curve, however, it appears that crystallization greatly enhances the S-shape.
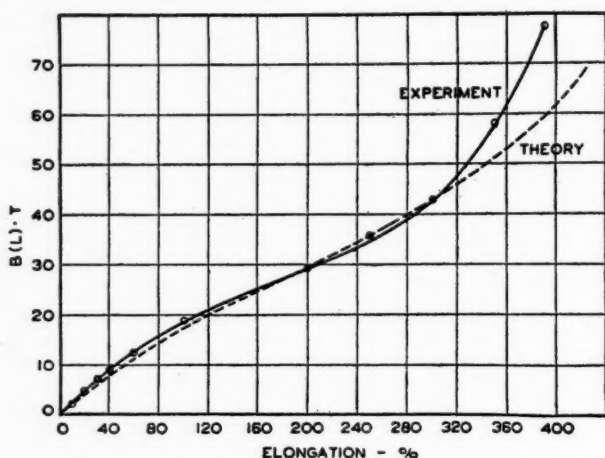


Fig. 9.—Plot of $B(L) \cdot T$ in arbitrary units against the elongation.

For clarity it seems worthwhile to note the fact that, although the terms "stress-strain curves" and "stress-temperature curves" are employed in this paper, these terms are not quite exact in the physical sense. The "stress" for the work presented here was determined by dividing the actual force at any temperature and elongation by the cross-sectional area of the unloaded sample, measured at room temperature after the run. The method of determining the relative length has been previously described. This manner of presenting the data conforms to that usually employed in literature on rubber. However, to avoid confusion it might seem more proper to substitute the terms "total force per square centimeter of cross-section of unloaded sample" in place of "stress", and "relative length" in place of "strain". In other words, the "stress-strain" curves presented here are really plots of total force *versus* relative length for a strip of rubber, the unloaded cross-section of which (at room temperature after the run) is 1 sq. cm.

In the comparison of our results with those of other investigations, the following points should be noted:

(1) With the exception of Wiegand and Snyder[9], the earlier investigators did not resolve the total force (or stress) into its additive parts due to internal energy and entropy. However, their experimental data are inadequate for this purpose. Moreover, even though they plot $F_u = \left( \dfrac{\partial U}{\partial L} \right)_T$, they plot

$$F_s/T = \left( \frac{\partial F}{\partial T} \right)_L \text{ instead of } F_s = T \left( \frac{\partial F}{\partial T} \right)_L.$$

(2) Our investigation is the first one which presents complete data on a particular compound for the region in which we are interested, *i.e.*, below the crystallization region.   Older data are partly inaccurate and partly wrong.

(3) We were the first to recognize correctly the influence of the volume thermal expansion on the equation of state.

(4) Comparison of our results with the statistical theory of James and Guth[2] permits us to infer that the retractive force in stressed rubber is predominantly of kinetic origin.

## SUMMARY

Summarizing, the following important conclusions may be drawn from these experiments on a typical unaccelerated soft gum compound.

1. The existence of the inversion point in the stress-temperature curves is shown to be due solely to ordinary volume thermal expansion, and may be eliminated by correcting for this thermal expansion.

2. The curves given in Figure 8a show that, for compounds of this type, the change of entropy with elongation accounts for more than 90 per cent of the total stress at room temperature, while the internal-energy contribution is less than 10 per cent and, to a first approximation, may be neglected.   In other words, the retractive force is due almost entirely to the tendency of the extended rubber molecules to return to a less ordered curled-up state.   This is in direct contrast to the elasticity exhibited by ordinary bodies, in which case elasticity is due to intermolecular forces.

3. The contribution of the entropy force to the total force is well represented by the theoretical expression of James and Guth[2].   This agreement constitutes our main reason for interpreting the entropy force as being due to the kinetic motion of the rubber molecules.

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# SPECIFIC HEAT OF THE SYNTHETIC RUBBER HYCAR–OR FROM 15° TO 340° K *

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## INTRODUCTION

The determination of the specific heat of Hycar-OR (oil-resistant) synthetic rubber is a continuation of a program started some years ago at the National Bureau of Standards, the object of which is to furnish thermodynamic data on various types of rubber, both natural and synthetic, and the monomers from which they are polymerized. Such data have been obtained for unvulcanized natural rubber[1] and its monomer, isoprene[2], and the equilibrium relationship between the two has been studied[3]. In the present paper, specific heat measurements on synthetic rubber Hycar-OR are described, and the increase in entropy from absolute zero to 25° C is calculated.

It has been found very useful in previous work to correlate thermal measurements with volume measurements. Anomalies in the enthalpy-temperature relation or its derivative are found to be associated with similar changes in the volume-temperature relation or its derivative. Measurements of the volume-temperature relation by means of a dilatometer, therefore, furnish a relatively simple method of determining the location of transitions and a guide for thermal measurements.

Volumetric work on several samples of synthetic rubber has shown that they, as well as natural rubber, may undergo transitions[4]. Two types of transition are found. In first-order transitions, the fundamental properties, such as enthalpy, undergo large changes in a rather narrow temperature interval. Crystallization and fusion are first-order transitions. In second-order transitions, the derivatives of the fundamental properties, rather than the properties themselves, undergo the large changes. The changes therefore manifest themselves in the expansivity and in the specific heat, which are the derivatives of the fundamental quantities, volume and enthalpy.

Natural rubber has been shown, both by thermal measurements[1] and dilatometric measurements[5], to exhibit both a first-order and a second-order transition. However, many of the synthetic rubbers, unlike natural rubber, show no evidence of crystallization or fusion. Since the crystallization of a rubber-like substance may make the thermal investigation very complicated and time-consuming[6], it was thought advisable to make thermal measurements first on a synthetic rubber which does not crystallize. Volume measurements[4] with a mercury-filled dilatometer have failed to show any evidence of crystallization or fusion in Hycar-OR, and it was selected for the first thermal studies. The volume measurements showed a second-order transition at 250° K.

## SAMPLE

Hycar-OR, samples of which we are indebted to the Hycar Chemical Co. of Akron, Ohio, is an oil-resistant, synthetic rubber which has been on the market since early in 1941. Its chemical composition has not yet been dis-

closed by the manufacturer, but it is reported to be a butadiene copolymer, and to contain about 2 per cent of phenyl-beta-naphthylamine as a stabilizer[7]. Some of the physical properties of the compounded Hycar are given by Garvey, Juve, and Sauser[8].

The density of a sample of unvulcanized Hycar-OR was found to be 0.999 gram per cubic centimeter at 25° C. An analysis of the material showed that it contained the following:

|  | Percentage |
|---|---|
| Carbon | 80.1 |
| Hydrogen | 9.3 |
| Nitrogen | 10.2 |
| Ash | 0.1 |
| Total | 99.7 |

Since practically the whole weight of the material, within experimental error, was accounted for in this manner, analytical determinations for other elements were not made. The carbon and the hydrogen were determined by the usual combustion technique, and the nitrogen by the Kjeldahl method.

Both the high nitrogen content and the oil-resistant properties of the polymer would lead to the conclusion that the comonomer used with the butadiene might be acrylonitrile. Since information is lacking as to the possible presence of other ingredients, and in view of the known ease of hydrolysis of nitriles, conclusions drawn from these figures as to the exact ratio of butadiene to acrylonitrile may be misleading.

The sample used for the specific-heat measurements was cut into small pieces, averaging about 5 to 10 cubic millimeters in volume. These small pieces were placed in the sample container of the calorimeter and kept under vacuum for several days to remove moisture and air. The container was then filled with helium at atmospheric pressure and 25° C, and sealed with solder. The weight of the dried sample was 30.030 grams.

## SPECIFIC HEAT

The calorimeter used for the measurements of specific heat was of the adiabatic vacuum-type described by Southard and Brickwedde[9]. It was similar to the apparatus previously used to determine the specific heat of rubber[1] and of isoprene[2], with some alterations intended to increase the convenience and facility of the measurements.

The results of all the measurements of specific heat are given, in chronological order, in Table I. The temperatures given in the table are the mean between the beginning and end temperatures for each heating. The values of $C_p$ were obtained from the equation given by Osborne, Stimson, Sligh, and Cragoe[10]:

$$[C_p]_{Tm} = \frac{\Delta Q}{\Delta T} - \left( \frac{\partial^2 C_p}{\partial T^2} \right)_{Tm} \frac{(\Delta T)^2}{24}$$

where $\Delta Q$ is the heat added per gram of sample, $\Delta T$ is the temperature rise, and $T_m$ is the mean temperature of the heating. However, the second term of the right-hand member of this equation was not significant except at temperatures between 238° and 251° K, in which region the second derivative of the specific heat with respect to temperature was large. At its maximum the last term in the equation amounted to about 2 per cent of the total. The

## TABLE I

### SPECIFIC HEAT VALUES (OBSERVED)

| Run No. | $T_m$ °K | $C_p$ j/g·°C[a] | Run No. | $T_m$ °K | $C_p$ j/g·°C[a] |
|---|---|---|---|---|---|
| I | 89.80 | 0.5545 | | 213.79 | 1.1221 |
| | 96.00 | .5965 | | 223.42 | 1.1688 |
| | 101.99 | .6250 | | 230.76 | 1.2068 |
| | 107.84 | .6527 | | 235.84 | 1.2388 |
| | 113.58 | .6782 | VI | 240.88 | 1.2708 |
| | 119.21 | .7070 | | 245.80 | 1.3517 |
| | 129.13 | .7505 | | 250.19 | 1.6996 |
| | | | | 254.47 | 1.8482 |
| | 92.95 | .5817 | | 258.52 | 1.8583 |
| | 104.84 | .6382 | | | |
| | 116.16 | .6929 | | 15.18 | 0.0728 |
| | 127.06 | .7437 | | 19.51 | .1046 |
| | 137.65 | .7914 | | 23.72 | .1383 |
| | 148.01 | .8353 | | 28.65 | .1777 |
| II | 158.19 | .8806 | | 33.35 | .2193 |
| | 168.21 | .9257 | | 39.78 | .2661 |
| | 178.08 | .9683 | | 47.68 | .3215 |
| | 187.82 | 1.0113 | VII | 55.08 | .3695 |
| | 197.45 | 1.0527 | | 61.98 | .4094 |
| | 206.98 | 1.0969 | | 65.62 | .4321 |
| | 216.39 | 1.1400 | | 68.88 | .4543 |
| | | | | 76.51 | .4942 |
| | 201.45 | 1.0670 | | 84.26 | .5364 |
| | 210.92 | 1.1117 | | 91.57 | .5746 |
| | 220.27 | 1.1553 | | 98.59 | .6065 |
| | 229.49 | 1.2024 | | | |
| III | 238.58 | 1.2565 | | 18.55 | .0982 |
| | 247.26 | 1.4161 | | 25.36 | .1522 |
| | 255.08 | 1.8471 | | 32.03 | .2074 |
| | 262.37 | 1.8698 | | 38.57 | .2588 |
| | 269.67 | 1.8903 | | 42.66 | .2865 |
| | | | VIII | 45.76 | .3075 |
| | 260.65 | 1.8621 | | 55.11 | .3690 |
| | 268.65 | 1.8841 | | 65.05 | .4305 |
| | 276.64 | 1.9126 | | 74.43 | .4810 |
| IV | 283.35 | 1.9304 | | 84.46 | .5368 |
| | 290.06 | 1.9478 | | 95.13 | .5907 |
| | 296.78 | 1.9675 | | | |
| | 303.51 | 1.9861 | | 283.92 | 1.9262 |
| | | | | 303.28 | 1.9740 |
| | 207.24 | 1.0932 | IX | 312.46 | 2.0042 |
| V | 228.42 | 1.1967 | | 322.53 | 2.0406 |
| | 237.71 | 1.2495 | | 333.52 | 2.0669 |
| | | | | | |
| | | | X | 310.85 | 2.0009 |

[a] Int. joules · gram⁻¹ · degree⁻¹.

temperature rise during a heating period was usually from 5 to 10 degrees, although this interval was considerably increased in a few instances where the specific heat-temperature curve was nearly linear, so that a larger temperature interval could be used without causing appreciable error. The rates of heating were varied from about 0.5° to 1.0° per minute. No consistent differences were observed between the data obtained from long heating intervals and those from short intervals, nor between the data obtained from rapid heating and those from slow heating.

The specific-heat data given in Table I are plotted in Figure 1. The broken line at the lowest temperatures is calculated from the Debye equation[11] for specific heats, with a value of 80 for the parameter $\beta\mu$. This value was selected because it was found to give the best agreement with the three lowest experimental points.
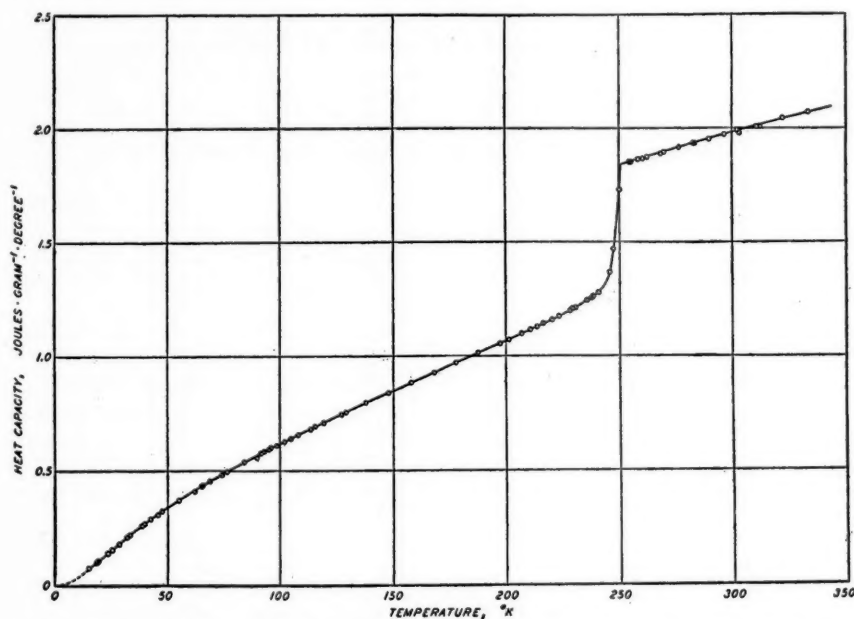


FIG. 1.—Relation between the heat capacity of Hycar-OR and temperature. The dotted part of the curve is calculated from the Debye equation.

The data from Table I were also used to prepare a large graph, in which $C_p/T$ values were plotted as a function of the temperature. Since, in the temperature range 18° to 340° K, the values of $C_p/T$ lie between 0.0052 and 0.0073 Int. joule·gram$^{-1}$·degree$^{-2}$, it was not difficult to plot the values on a scale sufficiently large to do justice to the accuracy of the data. From the best smooth curve drawn through the plotted values of $C_p/T$, values of $C_p$ were obtained at integral temperatures and are presented in Table II.

## THERMAL HISTORY

The temperature changes of the sample during the specific-heat measurements will be given in some detail, since it is possible that the results of this investigation may depend somewhat on the thermal history of the material. The first run was made after the sample had cooled quickly from room temperature to that of liquid air, about 85° K. Seven individual heatings in this run brought the temperature to 136° K. The sample was then cooled quickly again to 85° K and the second run was made, ending at 221° K. Next the sample was cooled by carbon dioxide snow to about 195° K. In the third run the temperature was raised to 273° K. At about 251° K (mean temperature of heating 247.26° K), the end of the sixth heating of this run, the tem-

## TABLE II

### SPECIFIC HEAT VALUES (FROM GRAPH)

| $T$ °K | $C_p$ j/g·°C[a] | $T$ °K | $C_p$ j/g·°C[a] | $T$ °K | $C_p$ j/g·°C[a] |
|---|---|---|---|---|---|
| 0  | 0.000[b] | 125 | 0.733 | 246 | 1.358 |
| 5  | .004[b]  | 130 | .756  | 247 | 1.402 |
| 10 | .030[b]  | 135 | .778  | 248 | 1.466 |
| 15 | .071     | 140 | .800  | 249 | 1.562 |
| 20 | .108     | 145 | .823  | 250 | 1.678 |
| 25 | .149     | 150 | .845  | 251 | 1.838 |
| 30 | .191     | 155 | .867  | 255 | 1.849 |
| 35 | .232     | 160 | .890  | 260 | 1.863 |
| 40 | .268     | 165 | .912  | 265 | 1.878 |
| 45 | .303     | 170 | .934  | 270 | 1.892 |
| 50 | .336     | 175 | .955  | 275 | 1.905 |
| 55 | .369     | 180 | .977  | 280 | 1.919 |
| 60 | .400     | 185 | .998  | 285 | 1.933 |
| 65 | .429     | 190 | 1.020 | 290 | 1.946 |
| 70 | .458     | 195 | 1.041 | 295 | 1.960 |
| 75 | .486     | 200 | 1.063 | 298.16 | 1.969 |
| 80 | .514     | 205 | 1.085 | 300 | 1.973 |
| 85 | .540     | 210 | 1.107 | 305 | 1.986 |
| 90 | .566     | 215 | 1.130 | 310 | 2.000 |
| 95 | .591     | 220 | 1.154 | 315 | 2.013 |
| 100 | .615    | 225 | 1.179 | 320 | 2.028 |
| 105 | .639    | 230 | 1.205 | 325 | 2.042 |
| 110 | .663    | 235 | 1.233 | 330 | 2.055 |
| 115 | .687    | 240 | 1.265 | 335 | 2.071 |
| 120 | .710    | 245 | 1.329 | 340 | 2.087 |

[a] Int. joules·gram$^{-1}$·degree$^{-1}$.
[b] Calculated from the Debye equation.

perature drifted downward at an initial rate of about one-thousandth of a degree per minute, under the usual adiabatic conditions. The drift continued for about 2 hours before it became inappreciable. At temperatures more than about 10 degrees above or below the second-order transition, the temperature became constant within a period of about 8 minutes after completion of a heating.

Overnight the temperature was allowed to rise to 287° K. From this temperature the specimen was cooled to 257° K, and during the fourth run the temperature was raised to 307° K. The specimen was cooled quickly again to 196° K for the fifth run. At about 246° K, the temperature at the end of the fourth heating of the run, a downward drift of temperature again took place. Before the temperature became constant, more heat was added until the temperature was 250° K.

The temperature was then allowed to decrease slowly by discontinuing the heating of the thermal shields around the sample container. The temperature fall was at the average rate of about 2.4° per hour. At 209° K the sixth run was started. Downward drifts of temperature were again observed at the ends of the fifth, sixth, and seventh heatings of this run, although only the normal time was required for equilibrium in all the other heatings. The approximate times required for a constant temperature to be reached after each of the three heatings just mentioned were 0.5 hour at 243° K, 1.5 hours at 248° K, and 1 hour at 252° K. From 260° K where the run ended, the

temperature was reduced slowly, reaching about 241° K in 16 hours. When subjected to adiabatic conditions after this treatment, the sample was found to drift upward slowly in temperature. The initial upward drift was about the same as the previous downward drifts, about a thousandth of a degree per minute. After about 2 hours no further change in temperature could be observed. The specimen was next heated to 254° K, and a downward drift of temperature was again observed.

The specimen was then allowed to come to room temperature, and remain at that temperature for several days. The temperature was next quickly lowered to 12.5° K, and the seventh run brought it up to 102° K. An immediate cooling brought the temperature to 21° K in preparation for the eighth run. After this run, the specimen was warmed to 217.5° K and a 50-minute heating, to be discussed in more detail later, raised the temperature to 270.2° K. After the sample had remained at room temperature overnight, the ninth run was made from 299° to 339° K. The tenth run included only one heating, which was from 299° to 323° K.

The 50-minute heating of the specimen from 217.5° to 270.2° K, mentioned in the previous paragraph, required 2.4 per cent less heat than that indicated by the curve of Figure 1. The third and sixth runs, on which the section of the curve near the transition is based, differed from each other by only 0.21 per cent over the range mentioned. If this 2.4-per cent discrepancy is real and not due to experimental error, it is probably connected with the time effect near the transition. The long drift in temperature before equilibrium near the transition should cause no error, since adiabatic conditions were maintained.

### ENTROPY

The entropy increase of Hycar-OR from 0° to 20° K was calculated from the Debye equation, using a $\beta\nu$ of 80. The value so obtained was:

$$S_{20} - S_0 = 0.056 \text{ Int. joule} \cdot \text{gram}^{-1} \cdot \text{degree}^{-1}.$$

The entropy change from 20° to 298.16° K was obtained from graphical integration of the curve $C_p/T$ against $T$, and gave:

$$S_{298.16} - S_{20} = 1.687 \text{ Int. joules} \cdot \text{gram}^{-1} \cdot \text{degree}^{-1}.$$

This value was also checked within experimental error by the integration of the $C_p$ versus log $T$ curve. The increase in entropy resulting from heating from the absolute zero of temperature to 25° C is calculated to be:

$$S_{298.16} - S_0 = 1.743 \pm 0.002 \text{ Int. joules} \cdot \text{gram}^{-1} \cdot \text{degree}^{-1}$$

(or $0.4167 \pm 0.0005$ calorie $\cdot$ gram$^{-1} \cdot$ degree$^{-1}$).[12] This value, with its probable error of 0.002, refers to the particular sample used under the conditions described.

### SUMMARY AND DISCUSSION

The specific-heat curve of Figure 1 shows a transition of the second order at about 250° K. During this transition, the specific heat increases abruptly by about 40 per cent, without the evolution or absorption of any heat. The transition first makes itself evident at about 225° K, where the specific-heat curve begins to deviate from the almost-linear increase which it has shown for over 100° below this temperature. Above 225° K the specific heat increases at an accelerated rate through the region of the transition. About one-half

the change of specific heat seems to occur between 249° and 251° K. The curve is drawn with a discontinuous slope at 251° K, since the results from several heatings which were begun just above 251° K showed no evidence of the transition, the points determined from them falling exactly on the linear curve.

A similar second-order transition is found in natural rubber at about 200° K, as has already been mentioned. Second-order transitions at widely different temperatures are found in many other substances of high molecular weight, such as styrene polymers[13], isobutene polymers[14], and methyl rubber[15]. Of the materials which have been studied, all of which have rubberlike properties have been found to have a second-order transition, and it is only above this transition temperature that such rubberlike properties have been observed. It seems likely that, at temperatures below that of the transition, no substance exhibits the extensibility and elasticity associated with natural rubber at normal temperatures.

The occurrence of a second-order transition of this type has been explained as resulting from a very slow approach to the equilibrium state at temperatures below the transition. On this view the location of the transition depends on the rate of temperature change; and at temperatures more than a few degrees below the transition, the times required for equilibrium are beyond the range of accessibility. Consequently at these temperatures one deals with a substance in an unstable state. Jenckel[16] studied the second-order transition in selenium at 30° C by volume measurements. He extended the measurements over the long periods of time which were necessary to reach equilibrium. Thus he was able to measure the rate of approach to equilibrium over a range of about 7° below the temperature at which the second-order transition occurs when the cooling is at the rate of more than a few tenths of a degree per minute. The drifts in temperature under adiabatic conditions, as described under the section on thermal history, may quite likely be explained on the basis of the slow approach to equilibrium. However, this point will not be discussed further, since it was not considered advisable at this time to make a detailed calorimetric study of the phenomenon.

Crystallization, a transition of the first order, is well known in natural rubber. In Hycar-OR, however, no evidence of it was found at any temperature. The failure of the atoms in this case to become part of an ordered crystalline structure is probably connected with the attachment of the nitrile groups to the main chain of the carbon atoms. Perhaps it is because of the size of the nitrile group, or perhaps it is because of the randomness of its position of attachment.

The specific-heat curve from 250° to 340° K is almost linear, so that the values of the specific heat for any temperature in this range may be calculated to within 0.2 per cent by means of the formula:

$$C_p = 0.00283T + 1.126,$$

in which $C_p$ is in Int. joules·gram$^{-1}$·degree$^{-1}$ and $T$ is the absolute temperature. The value at 298.16° K (25° C) is 1.971 Int. joules·gram$^{-1}$·degree$^{-1}$ (0.4712 calorie·gram$^{-1}$·degree$^{-1}$). This value is only slightly higher than that for natural rubber hydrocarbon, which is given as 1.880 Int. joules·gram$^{-1}$·degree$^{-1}$ [4].

The increase in entropy resulting from heating from the absolute zero of temperature to 298.16° K was found to be 1.743 Int. joules·gram$^{-1}$·degree$^{-1}$ for the Hycar, compared with 1.881 for natural rubber hydrocarbon.

Since the Hycar-OR was not in a crystalline state, it cannot be assumed, without further evidence, that the entropy at the absolute zero of temperature has a value of zero. However, since no significant difference in entropy could be found in the previously mentioned comparison of the amorphous and crystalline states of the natural rubber, it is possible that the same may be the case for the synthetic material.

## SUMMARY

Measurements of specific heat were made on a sample of Hycar-OR synthetic rubber from 15° to 340° K by means of an adiabatic vacuum-type calorimeter. The experimental values of the specific heat between 15° and 22° K were well represented by the Debye specific-heat equation, using a $\beta v$ value of 80 and, accordingly, the values below 15° K were calculated with this equation. At about 250° K the material has a transition of the second order, the specific heat increasing by about 40 per cent to a value of 1.84 Int. joules·gram$^{-1}$·degree$^{-1}$ just above the transition. From 250° to 340° K the specific heat-temperature curve is nearly linear, and the values can be calculated to within 0.2 per cent from the formula $C_p = 0.00283T + 1.126$, in Int. joules·gram$^{-1}$·degree$^{-1}$. At 298.16° K (25° C) the specific heat is 1.971 Int. joules·gram$^{-1}$·degree$^{-1}$ (0.4712 calories·gram$^{-1}$·degree$^{-1}$). The increase in entropy resulting from heating from 0° to 298.16° K was calculated to be 1.743 ± 0.002 Int. joules·gram$^{-1}$·degree$^{-1}$ (0.4167 ± 0.0005 calories·gram$^{-1}$·degree$^{-1}$).

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# VULCANIZATION OF LATEX. DIFFERENCES IN THE BEHAVIOR OF FRESH, OLD, AND PURIFIED LATEX [*]

J. W. van Dalfsen

## INTRODUCTION

After having studied the tensile strengths of unvulcanized latex films[1], it was decided to make a comparative study of various kinds of vulcanized latex films. In the new work vulcanization was effected on the one hand by the method of Schidrowitz[2], i.e., within the latex itself, and, on the other hand, by vulcanization of dried latex mixtures.

At the beginning of the investigation it was observed that, when vulcanized under certain conditions, fresh latex gives products which differ considerably from those obtained from identical conditions from old, preserved latex. This caused us to postpone the investigation as originally planned, and to study the vulcanization of latex in general and that of fresh latex in particular.

In the literature on the vulcanization of latex, there are no references to any differences in the behavior of old latex and fresh latex. For an extensive survey of the literature on the subject, the reader is referred to a work by Flint[3]; the few publications that have appeared since will be dealt with further on. The reader is referred also to brief work by van Dalfsen[4].

## METHODS EMPLOYED

The vulcanization of latex was followed for the most part by determining the mechanical properties (tensile strength, elongation at break, and modulus) of films obtained by evaporation. In most cases also, the structure of the coagulum obtained by the addition of formic acid was examined, and in numerous cases sulfur determinations were made, sometimes of the latex itself, in other cases of the latex films.

*Latex.*—In the experiments to be described, only latex from experimental plots of this institute (at Tjiomas) was used; but insofar as has been observed up to the present time, latex from other fields behaves in the same manner.

Immediately after collecting, the latex was ammoniated by adding 2 to 3.5 grams of $NH_3$ per liter; it reached the laboratory within 1–2 hours after having been ammoniated. In experiments which required the latex to be kept for a prolonged period, the ammonia content was increased to 6–7 grams per liter.

*Nomenclature of latex and latex films.*—The following scheme summarizes the various processes to which reference is made in this article, together with the products obtained.

*Dispersions.*—To disperse the vulcanization ingredients, they were rolled all of one night in a ball mill. To 1 gram of chemicals 1.5 cc. of water was added, and then 0.5 cc. of a 10 per cent ammonia-casein solution.

*Latex vulcanizations.*—In most of the experiments, various mixtures were vulcanized simultaneously so as to be able to compare their behavior. The

### FIELD LATEX

2 to 3.5 g. of $NH_3$ per liter of latex is added.

Ammoniated fresh latex

A dispersion of chemicals is added within 4 days after tapping.

The ammonia content is increased until it is 6–7 g. of $NH_3$ per liter.

| Vulcanization in the latex state | The mixture is evaporated | It is kept for longer than 4 days | It is creamed with creaming agents, or else it is concentrated by centrifuging. This is repeated, if required, after diluting the cream |
|---|---|---|---|
| Vulcanized fresh latex | Vulcanization of films in the dry state | | |
| Evaporation | | Old latex | Purified latex |
| Films produced by vulcanized fresh latex | Films from fresh latex vulcanized dry | | |
| | | Films are obtained in the same way as from fresh latex | |
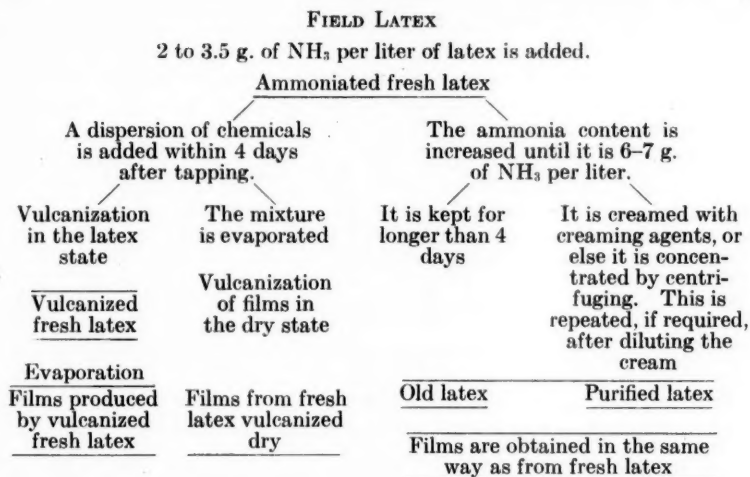
mixtures were not stirred during vulcanization, but the Erlenmeyer flasks containing the mixtures were shaken each half hour. Vulcanization was carried out in an electrically heated Inventum oven. As a rule the latex was not heated before the dispersion was added. The results are not to be regarded as a definite measure of the speed of the reaction; they are merely comparative within the one series.

Whenever, for the purpose of obtaining absolute data, it was intended to determine the speed of the reaction, vulcanization was carried out in a water bath, with agitation of both the latex and the water. The latex and also the dispersion of chemicals were raised to the reaction temperature before mixing.

*Depositing the films.*—The latex mixture, before being poured out, was left standing in a beaker to discover whether there was any settling of the chemicals, and to enable air-bubbles to escape. If there was any tendency on the part of the chemicals to settle, the viscosity was increased by adding at the most 1 per cent of Latekoll, based on the water content. Vulcanized latex was as a rule so viscous that it was necessary to dilute it to obtain films of uniform thickness.

After having increased or lowered the viscosity, the substance was poured out on level glass-plates, the edges of which had been smeared with vaseline. It was endeavored to obtain films having a thickness of 0.5 mm., but, in view of the fact that at the time of pouring the latex, the dry rubber had not in some cases been ascertained, so that it could not be precisely calculated how much latex was to be used, the thicknesses of the films were not the same. The admissible limits were taken to be 0.4 and 0.7 mm. For drying the poured latex, neither heating nor ventilation was applied. In all cases the films were removed from the plate two days after the latex had been poured out.

*Vulcanizing the films.*—The films were vulcanized in an Inventum oven, without resorting to artificial ventilation. The films were placed between filter paper.

*Tensile tests.*—The test-pieces and the Schopper tensile machine have already been described[1]. The test-pieces, the thicknesses of which had been measured, were first conditioned by placing them for 4 days over a saturated solution of ammonium chloride. In a few cases, other portions of the samples

were kept 4 days over silicagel (Bluegel).  Out of each sample, 6 test-pieces were obtained.

*Sulfur determinations.*—For determining free sulfur, both in latex and in dry rubber, the method of Oldham, Baker and Craytor[5] was followed; the modified method of Fowler[6] was also used.  Combined sulfur was calculated by deducting the free sulfur content from the free sulfur content, already determined; this was done immediately after adding the dispersion.

In this manner, no account was taken of the sulfur combined as sulfide (ZnS).  In the case of a few latex vulcanizates, however, it was found that this error did not exceed 0.2 per cent of sulfur.

## VULCANIZATION OF FRESH LATEX AT ROOM TEMPERATURE

Before any systematic experiments were made, it was observed that a latex mixture which contained, in addition to sulfur and zinc oxide, a dithiocarbamanate accelerator, yielded, after having been stored for several weeks and dried, rubber which at first sight appeared to be greatly overvulcanized.  Such rubber had very low tensile strength and extensibility, and showed almost no resistance to tearing; perhaps the word "short" or "brittle" best characterizes these properties.

In view of the patents of Schidrowitz[2], certain work by Davey[7], and the fact that vulcanized latex is used commercially for making rubber articles which without further vulcanization are ready for use, the above-mentioned observation was surprising.  But it was soon evident that fresh latex always behaves in this way in such a mixture and under such conditions.

Table 3 gives an example of the vulcanization of fresh latex.  For data concerning this latex, reference may be had to Table 1, while the composition

### TABLE 1
#### DATA ON THE LATICES REFERRED TO IN THE TABLES

| Latex No. | Pre-treatment of the latex | Age of the latex | Dry rubber content | Modulus (kg. per sq. cm.) | Hydrogen (percentage) | Ash (percentage) |
|---|---|---|---|---|---|---|
| | | | | | on crepe | |
| 1 | none | some hours | 46.0 | ? | | |
| 2 | none | some hours | 34.9 | 37.8 | | |
| 3 | none | some hours | 34.0 | 36.5 | 0.42 | 0.21 |
| 4 | purified twice | 14 days | 50.6 | 50.7 | 0.05 | 0.09 |
| 5 | none | some hours | 38.0 | 40.5 | | |
| 6 | creamed 4 times | 1½ hours | 48.0 | 48.2 | | |
| 7 | = latex No. 6 | 3 months | 48.0 | 48.2 | | |
| 8 | none | some hours | 33.7 | 36.2 | | |
| 9 | none | some hours | 35.9 | 38.8 | | |
| 10 | none | some hours | 37.9 | 40.3 | | |
| 11 | none | some hours | 36.6 | 39.5 | | |

### TABLE 2
#### LATEX COMPOUNDS REFERRED TO IN THE TABLES

| Compounds | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Rubber, as latex | 100.0 | 100.0 | 100.0 | 100.0 | 100 |
| Zinc oxide | 2.0 | 2.0 | 1.5 | 2.0 | ... |
| Sulfur | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Vulcafor-SDC | ... | 0.8 | 0.8 | ... | ... |
| Vulkacit-P Extra N | 0.8 | ... | ... | ... | ... |
| Agerite powder | 1.0 | ... | ... | ... | ... |
| Vulcafor-ZDC | ... | ... | ... | 1.0 | 1.0 |

TABLE 3

FRESH LATEX VULCANIZED AT ROOM TEMPERATURE

Compound 1; latex 1.

| Days in storage | Viscosity at 30° C (centipoises) | Combined sulfur in the latex | Tensile strength (kg. per sq. cm.) | Elongation at break (percentage) | Modulus (stress at 600% elongation in kg. per sq. cm.) |
|---|---|---|---|---|---|
| | | | Mechanical properties of the films (relative humidity of 79 per cent) | | |
| 0 | 9.0 | 0.0 | .. | ... | .. |
| 1 | 10.8 | 0.0 | 3 | 896 | 2 |
| 2 | 11.1 | 0.0 | 12 | 984 | 4 |
| 3 | 16.1 | 0.1 | 20 | 970 | 6 |
| 4 | 19.2 | 0.1 | 31 | 982 | 8 |
| 5 | 21.6 | 0.2 | 38 | 971 | 10 |
| 7 | 24.1 | 0.2 | 41 | 904 | 14 |
| 10 | 24.6 | 0.4 | 44 | 810 | 19 |
| 14 | 24.8 | 0.6 | 36 | 723 | 20 |
| 21 | 25.1 | 1.0 | 29 | 625 | 24 |
| 28 | ... | (1.2)* | film is brittle; no determinations | | |

\* In the rubber.

of the mixture is given in Table 2. It is clear that as combination of sulfur proceeds, an increase in the tensile strength of the latex films is first noticed, but after only 10 days' storage the mixture shows a regression. This would not be surprising were it not that the optimal mechanical properties of the rubber were so poor that one could not really speak of a properly vulcanized product. Rubber obtained from this latex mixture, after the latter had been kept for upwards of 10 days, showed increasing overvulcanization, until, after 28 days (the conclusion of our observation), films were obtained that had no tensile strength to speak of. Therefore, although this behavior points to overvulcanization, it is evident (see Table 4) that, by subsequent dry vulcani-

TABLE 4

ADDITIONAL VULCANIZATION OF FILMS FROM VULCANIZING LATEX STORED 28 DAYS AT ROOM TEMPERATURE

| Vulcanization (min. at 90° C) | Combined sulfur in the rubber (percentage) | Tensile strength (kg. per sq. cm.) | Elongation at break (percentage) | Modulus (stress at 600% elongation in kg. per sq. cm.) |
|---|---|---|---|---|
| | | Mechanical properties of the films (relative humidity of 79 per cent) | | |
| 20 | 1.4 | 93 | 640 | 72 |
| 45 | 1.5 | 165 | 615 | 152 |
| 90 | ... | 152 | 628 | 125 |

zation of the rubber, even of that obtained from a latex mixture that had been kept 28 days, there is considerable improvement in its mechanical properties. Hence it is clear that there is no question whatever of overvulcanization in the usual sense.

Attention should be called to the fact that the mechanical properties of the rubber were determined after it had been kept one week over a saturated solution of ammonium chloride, i.e., at a relative humidity of 79 per cent. A study of the mechanical properties of unvulcanized latex films showed that by drying a considerably higher tensile strength is obtained, while Table 5 shows that films obtained from vulcanized fresh latex also are rendered stronger by drying. The difference between the effect obtained by subsequent vul-

TABLE 5

REVERSIBILITY OF THE EFFECT OF DRYING ON THE MECHANICAL PROPERTIES OF
FILMS FROM VULCANIZED FRESH LATEX
MECHANICAL PROPERTIES OF AN UNCURED FILM FROM THE LATEX

| Relative humidity (percentage) | Tensile strength (kg. per sq. cm.) | Elongation at break (percentage) | Modulus (stress at 600% elongation in kg. per sq. cm.) |
| --- | --- | --- | --- |
| 79 | 92 | 1036 | 9 |
| 0.0 | 181 | 842 | 66 |

Compound 2.
Latex 2.
Vulcanized 2 hours at 80° C.

FILMS FROM VULCANIZED FRESH LATEX

(r.h. = relative humidity; TSB = tensile strength in kg. per sq. cm.;
EB = elongation in percentage at break)
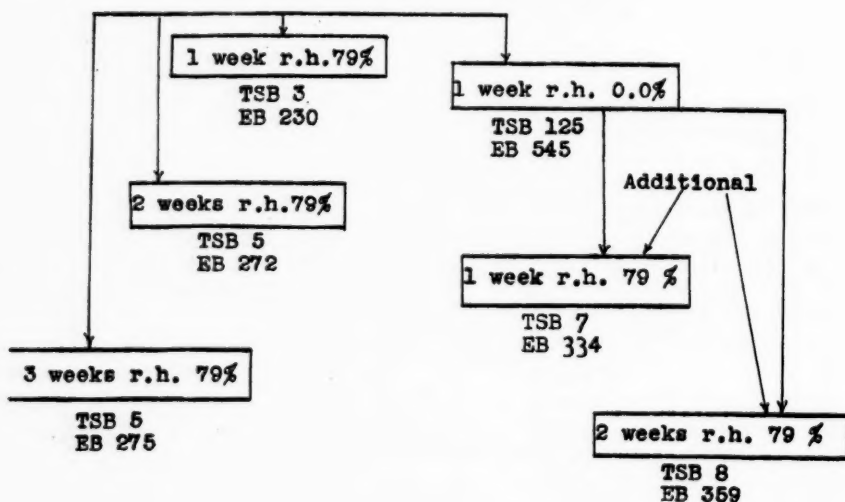


canization and that obtained by desiccation is obviously due to the fact that
by drying only a reversible increase of the tensile strength is produced, which
disappears again in a humid atmosphere (see Table 5), whereas, by subsequent
dry vulcanization, irreversible strengthening is produced.

The short latex films obtained from the latex mixture 28 days old exhibited,
in addition to their brittleness, other properties abnormal to vulcanized rubber;
this matter will be dealt with at length a little further on. Also it was found
that when acid was added, the 28 days' old latex mixture did not coagulate
but only flocculated. This led us to study the behavior, in subsequent vul-
canization tests, of the latex mixture when acid was added.

In view of the abnormally poor mechanical properties of rubber obtained
from self-vulcanizing latex, two problems present themselves. First, the ques-
tion may be asked whether this phenomenon always occurs in fresh latex,
even when the conditions of vulcanization differ with respect to temperature,
vulcanizing ingredients, stabilizers, etc. We shall endeavor to answer this
question a little further on. In the second place, the question arises as to

what extent good mechanical properties can be obtained by the dry vulcanization of films from such mixtures of fresh unvulcanized latex. Let it suffice here to state that such mixtures give films with entirely normal tensile strengths at relative humidity of 79 per cent.

With reference to the observation that the moisture content affects greatly the tensile strengths of films obtained from vulcanized fresh latex, it may be noted that Flint and Naunton[8] found indications that pointed in the same direction. These investigators determined the tensile strengths of such films by inflating them until they tore, using both air and water for applying the necessary pressure. They state that dry-vulcanized films gave the same values, whether water pressure or air pressure was applied. Films obtained from vulcanized latex also gave the same values under the two conditions, provided the latex contained a volatile alkaline preservative. In the presence of a non-volatile alkaline preservative, the determination by means of water pressure gave considerably lower results. By supplementary dry vulcanization this sensitivity to water can be eliminated. Contrary to these observations, we found also that when ammonia is used as a preservative, the films obtained from vulcanized fresh latex are exceptionally sensitive to the presence of moisture. This contradiction can be readily explained by the fact that we worked with fresh latex, which obviously was not at the disposal of Flint and Naunton[8].

## VULCANIZATION OF FRESH LATEX AND OF PURIFIED LATEX

When vulcanized as described in the preceding section, fresh latex behaves in the same way that it does when it is vulcanized with zinc oxide and an ultra-accelerator at higher temperatures, but below 100° C. In subsequent tests, which are summarized in Tables 6 and 7, the behavior of fresh latex was compared with that of purified latex, about 14 days old, prepared from it, vulcanization being effected at 80° C. In view of the unavoidable difference in the age of the latices, the vulcanization tests could not be carried out simultaneously, but care was taken that the conditions were identical. Heating was carried out with stirring in a water bath, the temperature of which was kept constant to ±5° C. The latex and the dispersion were brought separately to 80° C before they were mixed.

The latex was purified by repeated centrifuging, alternated by diluting, of the original fresh latex. Purification was carried further by an artifice, based on physical means, concerning which no further particulars can be communicated at this time, since it is the subject of Netherlands patent application, No. 92,872, submitted by the Central Association of Experimental Stations, and which in time will be accessible. The degree to which the latex was purified is shown in Table I.

The rubber obtained from fresh latex at the relative humidity of 79 per cent apparently did not at any moment during its vulcanization attain any tensile strength worth mentioning. Its vulcanization as latex reduces its tensile strength elongation at rupture. Plastic rubber, therefore, changes to brittle, overvulcanized rubber. When dry, a considerably higher tensile strength is obtained, although even this is greatly below that of rubber from vulcanized purified latex under the same conditions. At 79 per cent relative humidity, this last rubber has a fairly high tensile strength. The tensile strength and elongation are shown in Figure 1. Attention is called to the high modulus of rubber from vulcanized fresh latex in its dry state.

TABLE 6

Compound 3.

VULCANIZATION AT 80° C OF FRESH LATEX AND OF PURIFIED LATEX OBTAINED FROM THIS LATEX

| Vulcanizing time (min.) | Combined sulfur in the latex and in the dry film, respectively | | Latex 3, fresh — Mechanical properties of the films (at relative humidities of 79 and 0 per cent, respectively) | | | | | | Combined sulfur in the latex and in the dry film, respectively | | Latex 4, purified — Mechanical properties of the films (at relative humidities of 79 and 0 per cent, respectively) | | | | | | Structure of the coagulum | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Tensile strength (kg. per sq. cm.) | | Elongation at break (percentage) | | Modulus (kg. per sq. cm. at 600% elongation) | | | | Tensile strength (kg. per sq. cm.) | | Elongation at break (percentage) | | Modulus (kg. per sq. cm. at 600% elongation) | | Fresh latex | Purified latex |
| 0 | 0.00 | 0.36 | 71 | 188 | 1003 | 863 | 7 | 65 | 0.00 | 0.66 | 109 | 126 | 998 | 1029 | 7 | 14 | normal | normal |
| 5 | 0.11 | 0.44 | 66 | 271 | 999 | 912 | 10 | 85 | 0.03 | 0.72 | 140 | 164 | 979 | 1009 | 9 | 13 | normal | normal |
| 10 | 0.26 | 0.47 | 48 | 292 | 879 | 873 | 11 | 95 | 0.07 | 0.72 | 195 | 200 | 1041 | 982 | 10 | 18 | normal | normal |
| 15 | 0.32 | 0.46 | 41 | 295 | 844 | 837 | 11 | 110 | 0.10 | 0.69 | 251 | 240 | 1035 | 1020 | 14 | 17 | normal | normal |
| 20 | 0.40 | 0.62 | 30 | 285 | 773 | 817 | 11 | 105 | 0.19 | 0.79 | 262 | 293 | 988 | 1052 | 20 | 17 | normal | normal |
| 30 | 0.59 | 0.74 | 30 | 221 | 725 | 739 | 13 | 105 | 0.29 | 0.85 | 303 | 348 | 1000 | 1023 | 20 | 22 | short | short |
| 45 | 0.87 | 1.07 | 28 | 194 | 684 | 697 | 15 | 105 | 0.42 | 1.00 | 302 | 350 | 965 | 963 | 23 | 27 | short | short |
| 60 | 1.05 | 1.15 | 24 | 187 | 614 | 651 | 18 | 120 | 0.63 | 1.08 | 302 | 353 | 915 | 940 | 33 | 35 | flocculent | short |
| 75 | 1.25 | 1.34 | 16 | 161 | 498 | 603 | 16 | 135 | 0.80 | 1.12 | 255 | 321 | 870 | 891 | 34 | 43 | flocculent | granulated |
| 90 | 1.35 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | pasty | granulated |
| 150 | ... | ... | ... | ... | ... | ... | ... | ... | 1.29 | 1.54 | 221 | 257 | 763 | 772 | 59 | 67 | pasty | granulated |

## Table 7

### Supplementary Dry Vulcanization of Films Obtained from Fresh and from Purified Latex Vulcanized at 80° C

Mechanical properties of films (79 and 0 per cent relative humidities)

| Time of dry vulcanization at 110° C (min.) | Films from vulcanized fresh latex | | | | | | Films from vulcanized purified latex | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Tensile strength (kg. per sq. cm.) | | Elongation at break (percentage) | | Modulus (stress in kg. per sq. cm. at 600% elongation) | | Tensile strength (kg. per sq. cm.) | | Elongation at break (percentage) | | Modulus (stress in kg. per sq. cm. at 600% elongation) | |
| | 79% | 0% | 79% | 0% | 79% | 0% | 79% | 0% | 79% | 0% | 79% | 0% |
| **After 15 min. vulcanization in latex state** | | | | | | | | | | | | |
| 0 | 41 | 295 | 844 | 837 | 11 | 110 | 251 | 240 | 1035 | 1020 | 14 | 17 |
| 5 | 144 | 326 | 920 | 868 | 21 | 111 | 398 | 401 | 1005 | 1038 | 22 | 28 |
| 10 | 179 | 345 | 923 | 863 | 22 | 113 | 409 | 405 | 1031 | 1037 | 25 | 27 |
| 15 | 205 | 326 | 908 | 849 | 22 | 104 | 394 | 376 | 996 | 1003 | 23 | 22 |
| 30 | 218 | 334 | 922 | 878 | 18 | 87 | 308 | 302 | 1038 | 1030 | 17 | 21 |
| 45 | 214 | 356 | 969 | 904 | 17 | 77 | 135 | 150 | 1022 | 1023 | 11 | 16 |
| **After 75 min. vulcanization in latex state** | | | | | | | | | | | | |
| 0 | 16 | 161 | 498 | 603 | 16 | 135 | 255 | 321 | 870 | 891 | 34 | 43 |
| 5 | 69 | 187 | 660 | 623 | 39 | 159 | 333 | 357 | 894 | 895 | 42 | 43 |
| 10 | 88 | 212 | 680 | 646 | 42 | 150 | 331 | 364 | 882 | 928 | 33 | 32 |
| 15 | 118 | 220 | 709 | 662 | 45 | 143 | 342 | 365 | 953 | 952 | 29 | 27 |
| 30 | 133 | 250 | 719 | 693 | 37 | 145 | 360 | 366 | 958 | 984 | 30 | 26 |
| 45 | 152 | 251 | 768 | 723 | 25 | 112 | 213 | 245 | 942 | 982 | 21 | 20 |

GRAPH I.—The tensile strength and elongation at break of films from fresh field-latex and purified latex, both vulcanized at increasing periods, and the influence of a supplementary dry vulcanization on some of these films (see Tables 6 and 7).

The combined sulfur in the latices varies. Fresh latex vulcanizes more rapidly, especially at first. However, vulcanization of the purified latex was continued until about the same percentage of sulfur had combined as in the fresh latex. The great difference in the mechanical properties, therefore, cannot be explained by different percentages of combined sulfur in the latex stage. Table 6 also indicates the percentages of combined sulfur in the films at the moment of pulling. These data show a few irregularities; it is probable that films from purified latex vulcanized a short while vulcanize more thoroughly and rapidly in a dry state than does the corresponding rubber from fresh latex. The differences in the behavior on additional vulcanization in the dry state, however, are not great enough to explain the difference in the mechanical properties of rubber from these two latices.

Finally attention should be called to the column in Table 6 headed "structure of the coagulum". As vulcanization proceeds, purified latex gradually changes, as is manifest in the coagulum when an acid is added. The coherence of the coagulum gradually decreases, and it becomes more brittle. This gradual change is expressed in the table by the words "normal", "short", and "granular". In this last stage, the fresh coagulum is so little cohesive that it can be reduced to granules by means of a stirring rod. However, if it is not stirred after acid has been added, it remains a coherent coagulum, even if vulcanization is continued. Perhaps theoretically it is possible that a purified latex by very prolonged vulcanization may ultimately flocculate when an acid is added, but despite numerous tests we have never succeeded in realizing this. When heating is continued for a very long time, coagulation usually sets in.

The changes in the behavior of fresh latex when an acid is added during vulcanization are essentially different. In this case the coherence and elasticity of the coagulum gradually decline as combination of sulfur proceeds; instead of brittle grains, however, flakes are obtained after vulcanizing about one hour. Beyond this point, no coherent coagulum is obtained, but a flocculate. This flocculate is reversible and, when rubbed between thumb and finger, it becomes a paste, without the particles clotting. At this stage, vulcanized fresh latex can in no way be transformed into a coherent coagulum, either by chemical or by mechanical means. This offers possibilities of application where ordinary latex, through its range of stability[9], falls short or offers difficulties. Thus vulcanized fresh latex can be mixed in any proportion with cement without the necessity of adding any stabilizers and without coagulation setting in. Should such applications be considered, it must be fully realized that this particular form of latex is not sticky.

The characteristic properties of vulcanized fresh latex will be retained on keeping for a few months; when necessary excessive undissolved sulfur can be removed by clarification to prevent any tendency to autovulcanization.

Table 7 shows that films obtained from vulcanized fresh latex, which exhibit such short or brittle characteristics when moisture is present, are not overvulcanized. Subsequent dry vulcanization at 110° C increases the tensile strength and the elongation at break. Although this phenomenon is most evident when the films are moist, this strengthening effect is also noticeable in dry films. Furthermore, films prepared from vulcanized purified latex are strengthened by subsequent dry vulcanization; however, when vulcanization is too prolonged, overcuring results. Despite the fact that films obtained from vulcanized fresh latex contain more combined sulfur at the moment that the subsequent dry vulcanization is applied, they show later a tendency to overcure. A few observations concerning the effect of such supplementary dry vulcanization are shown graphically in Figure 1.

## EFFECT ON VULCANIZATION OF THE QUANTITY AND THE NATURE OF THE SERUM COMPONENTS

From the experiments described, which were made with ordinary fresh latex and with highly purified, older latex, it is highly probable that the quantity of serum components largely determines the mechanical properties of the rubber obtained after vulcanization in the latex state. This is confirmed by subsequent experiments, the results of which are compiled in Tables 8 and 9.

### TABLE 8

#### VULCANIZATION OF MIXTURES OF PURIFIED AND FRESH LATEX

Latices 5 and 7; compound 3.

Properties after 5 hours' vulcanization at 80° C

| Composition of the mixture in percentage of TS rubber | | Mechanical properties of the films (relative humidity of 79 per cent) | | | | |
|---|---|---|---|---|---|---|
| Latex creamed 4 times* | Fresh latex | Tensile strength (kg. per sq. cm.) | Elongation at break (percent-age) | Modulus (stress in kg. per sq. cm. at 600% elongation) | Combined sulfur in the films (percentage) | Structure of the coagulum |
| 100 | .. | 163 | 731 | 53 | 1.6 | normal |
| 75 | 25 | 112 | 715 | 48 | 1.5 | short |
| 50 | 50 | 18 | 393 | .. | 1.6 | granulated |
| 25 | 75 | 11 | 283 | .. | 1.5 | flaked |
| .. | 100 | 5 | 88 | .. | 1.7 | pasty |

* The creaming was effected in accordance with the process described in Netherlands Patent No. 37,288, issued to the Central Association of Experimental Stations.

### TABLE 9

#### VULCANIZATION OF PURIFIED LATEX AS SUCH AND TO WHICH SERUM FROM FRESH LATEX HAS BEEN ADDED

Latex 6; compound 3.

| Latex | Vulcanized (hours at 80° C) | Mechanical properties of the films (relative humidity of 79 per cent) | | | | |
|---|---|---|---|---|---|---|
| | | Tensile strength (kg. per sq. cm.) | Elongation at break (percent-age) | Modulus (stress in kg. per sq. cm. at 600% elongation) | Combined sulfur in the films | Structure of the coagulum |
| Latex creamed 4 times | 5 | 181 | 778 | 51 | 1.5 | normal |
| | 10 | 134 | 732 | 59 | 1.6 | short |
| | 24 | 121 | 682 | 65 | 1.6 | short |
| Serum of fresh latex added | 5 | 157 | 713 | 71 | 1.6 | short |
| | 10 | 41 | 493 | .. | 1.7 | flaked |
| | 24 | none | none | .. | 1.8 | pasty |

Mixtures of latex creamed four times and fresh latex in different proportions were simultaneously heated under identical conditions. After vulcanization for 5 hours, the mixtures were poured out; the mechanical properties of the rubber obtained were determined at the relative humidity of 79 per cent. The differences in the percentages of combined sulfur proved to be insignificant. It is apparent that there is a gradual transition of the properties of the fresh latex to those of the purified latex, both with respect to mechanical properties and structure of the coagulum.

Finally to make sure that the difference in the behavior of fresh and of purified latex is the result of differences in the serum components and not differences in the rubber hydrocarbon, the following test was applied. Purified latex was vulcanized after adding serum obtained from fresh latex by coagu-

lating the latter with the aid of cement and aluminum chloride. The serum was ammoniated, decalcified by ammonium oxalate, and filtered. Evidently it is not sufficient to add these substances to make purified latex behave like fresh latex, but it is clear that its properties undergo changes in the direction of those of fresh latex.

The result of vulcanizing purified latex is practically not affected by adding casein, peptone, or lecithin.

In the foregoing experiments, the quantities of various serum components were determined with reference to purified latex. The nature of the various serum components greatly affects the vulcanization of latex. This is evident from tests, the results of which are summarized in Table 10. Fresh latex was divided into three parts, which were preserved with 5, 10, and 20 grams, respectively, of $NH_3$ per liter. Even on vulcanization when still fresh, latex to which 20 grams of $NH_3$ per liter had been added yielded a rubber with better mechanical properties at 79 per cent relative humidity than was obtained with a lesser ammonia content. When the ammonia content was higher, combination of sulfur proceeded a little more slowly. After having been kept for 1 week and for 5 weeks, respectively, it was again vulcanized. Combination of sulfur progressed more slowly than it did with fresh latex, while the tensile strength of the rubber at 79 per cent relative humidity was higher than that produced by vulcanization when fresh. During storage, therefore, the vulcanizing properties of ordinary latex change in the direction of those of purified latex.

## CHOICE OF MIXTURE; CONDITIONS GOVERNING VULCANIZATION

In discussing the results shown in Table 10, attention has already been drawn to the difference in behavior of vulcanized fresh latices containing successively larger proportions of ammonia. Since it was found that, on storage of ammoniated latex, the results of the latex vulcanization changed in the sense that, at 79 per cent relative humidity, a higher tensile strength was obtained and that no real flocculation takes place when an acid is being added, it is evident that hydrolysis of the serum components, which is the most probable cause of this phenomenon, can also make its influence felt during vulcanization.

It was, in fact, found that if the conditions of vulcanization are such that hydrolysis of the serum components is promoted, the effects gradually approximate those obtained with purified latex.

Hydrolysis is promoted by vulcanizing:

(1) at a higher temperature for the same length of time;
(2) for a longer time at the same temperature;
(3) in a mixture having a higher pH value.

The effect produced by (1) can be verified by vulcanizing fresh latex in an autoclave at 145° C. We did not succeed in attaining a state at which flocculation occurred by the addition of an acid; at the most a coagulate with a granular consistency, but with little coherence, was obtained. Nor can a flocculate be obtained if no ultra-accelerators are used at a vulcanization temperature below 100° C. In all cases we were able, by adding an acid, to obtain a flocculate with each of the ultra-accelerators tried, provided also that zinc oxide was present. Whether during vulcanization the ultra-accelerator dissolves readily in water does not appear to play a part, for Vulcafor-SDC (dissolving readily), Vulcafor-ZDC (dissolving poorly), Vulcafor-TET (dis-

## TABLE 10

CHANGES IN THE VULCANIZING PROPERTIES OF LATEX PRESERVED WITH INCREASING PERCENTAGES OF AMMONIA

Latex 8; part I contains 5 grams of NH₃ per liter.
II contains 10 grams of NH₃ per liter.
III contains 20 grams of NH₃ per liter.
Compound 2.

Mechanical properties of the films at relative humidity of 79 per cent

| Age of the latex | Time of vulcanization at 80° C (hours) | Tensile strength (kg. per sq. cm.) | | | Elongation at break (percentage) | | | Modulus (stress in kg. per sq. cm. at 600% elongation) | | | Combined sulfur in the films (percentage) | | | Structure of the coagulum | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | I | II | III | I | II | III | I | II | III | I | II | III | I | II | III |
| 1 day | 1 | 3 | 6 | 6 | 829 | 936 | 948 | 2 | 2 | 2 | 0.8 | 0.8 | 0.8 | normal | normal | normal |
| | 3 | 8 | 19 | 36 | 495 | 805 | 973 | : | 9 | 9 | 0.9 | 0.7 | 0.7 | short | short | short |
| | 5 | 4 | 9 | 53 | 77 | 301 | 725 | : | : | 25 | 1.6 | 1.4 | 1.2 | pasty | flaky | short |
| 1 week | 1 | 90 | 99 | 149 | 1118 | 1180 | 1190 | 8 | 9 | 12 | 0.9 | 0.7 | 1.0 | normal | normal | normal |
| | 3 | 144 | 149 | 188 | 858 | 962 | 1027 | 29 | 22 | 19 | 0.9 | 0.8 | 0.9 | normal | normal | normal |
| | 5 | coag. | 96 | 147 | coag. | 717 | 828 | : | 43 | 31 | : | 1.4 | 1.0 | : | short | short |
| | 10 | coag. | 10 | 36 | coag. | 187 | 573 | : | : | : | : | : | 1.6 | : | granular | granular |
| 3 weeks | 3 | coag. | 142 | 127 | coag. | 800 | 889 | : | 23 | 21 | : | 0.9 | 1.0 | : | normal | normal |
| | 5 | coag. | 137 | 147 | coag. | 855 | 916 | : | 27 | 25 | : | 1.0 | 1.0 | : | normal | short |
| | 10 | coag. | 48 | 56 | coag. | 609 | 956 | : | 41 | 33 | : | 1.5 | 1.2 | : | short | normal |
| | 24 | coag. | none | none | coag. | none | none | : | : | : | : | 1.8 | 1.8 | : | granular | granular |

solving readily), and Vulcacit-P Extra N (dissolving poorly) gave the same results. When the mixture contained no zinc oxide, combination of sulfur proceeded much more slowly; the rubber at 79 per cent relative humidity had a higher tensile strength, nor was it possible to obtain a flocculate by adding acid. Curiously enough, Vulcafor-ZDC behaves in the presence or absence of zinc oxide in the same way as do other ultra-accelerators. Therefore, the action of Vulcafor-ZDC during the vulcanization of latex is not the same as, for example, that of Vulcafor + SDC + zinc oxide, which is the case in ordinary dry vulcanization. To what extent Vulcafor-ZDC is activated by zinc oxide during the vulcanization of latex is evident from the following test. Vulcanization was carried out with the same latex under the same conditions, except in one case in the presence of sulfur, zinc oxide, and Vulcafor-ZDC; in the other case with the same mixture but with no zinc oxide. When zinc oxide was present, vulcanization for 5 hours at 80° C gave a product containing 1.6 per cent of combined sulfur whereas, in the absence of zinc oxide, only 0.6 per cent of sulfur combined. As is evident from Table 11, which gives

TABLE 11

ACTIVATING EFFECT OF ZINC OXIDE ON VULCAFOR-ZDC AS AN ACCELERATOR
IN LATEX VULCANIZATION

Latex 9; compounds 4 and 5.

Properties of the films (relative humidity of 79 per cent)

| | Without zinc oxide | | | | Zinx oxide present | | | |
|---|---|---|---|---|---|---|---|---|
| Vulcani-zation at 80° C (hours) | Tensile strength (kg. per sq. cm.) | Elongation at break (percent-age) | Modulus (stress in kg. per sq. cm. at 600% elongation) | Com-bined sulfur (percent-age) | Tensile strength (kg. per sq. cm.) | Elongation at break (percent-age) | Modulus (stress in kg. per sq. cm. at 600% elongation) | Com-bined sulfur (percent-age) |
| 0 | 14 | 980 | 4 | 0.4 | 17 | 932 | 3 | 0.6 |
| 1 | 25 | 995 | 6 | 0.4 | 7 | 959 | 4 | 0.7 |
| 2 | 50 | 891 | 12 | 0.5 | 36 | 987 | 8 | 0.8 |
| 3 | 74 | 892 | 19 | 0.5 | 31 | 774 | 15 | 0.8 |
| 4 | 83 | 953 | 16 | 0.6 | 12 | 400 | .. | 1.2 |
| 5 | 88 | 996 | 13 | 0.6 | 7 | 177 | .. | 1.6 |

the results of these tests in detail, the mechanical properties of the rubber conformed to this entirely different vulcanization. At 79 per cent relative humidity, the rubber obtained from latex vulcanized for 5 hours without zinc oxide was plastic (with a high elongation at break and a low tensile strength) whereas, under identical conditions, but in the presence of zinc oxide, a brittle product was obtained (with a still lower tensile strength and a very low elongation at break).

The stage in the vulcanization of latex at which a flocculate is obtained by addition of an acid seems to be governed by the presence of zinc oxide, although it does not follow from these tests that the function of zinc oxide is confined to acceleration, i.e., that it would prevent excessive hydrolysis resulting from prolonged vulcanization, or that it performs some other function, such as reacting with the serum components.

It was also attempted to substitute other oxides and metal salts for zinc oxide. Experiments were carried out with the oxides of magnesium and lead and with ammonia complexes of nickel, cobalt, cadmium and copper. None of these metal compounds enhanced the activity of any ultra-accelerator during the vulcanization of fresh latex at 80° C to any appreciable extent[10].

It is possible to substitute other zinc compounds for zinc oxide, provided they are soluble in latex. It is assumed that zinc, in the form of zinc-ammonia complexes, is present in ammoniated latex. But experiments show that not more than 5 mg. of zinc oxide per 100 cc. of water was present in solution in water containing 5 grams of NH₃ per liter after having been heated for 4 hours at 80° C. In latex having a corresponding ammonia content, therefore, only 10 mg. of zinc oxide per 100 grams of rubber would be present in solution. But it was found that if the quantity of zinc oxide added is reduced to less than 1.5 grams per 100 grams of rubber, vulcanization is retarded. This suggests that zinc oxide is not merely an activator of the accelerator, but also that it is consumed during vulcanization, either in the form of an ammonia complex or as zinc oxide itself.

The effect of the pH value on the vulcanization of latex was not investigated systematically. Summarizing the various data obtained, the impression is gained that, as the pH value increases (by adding KOH or NaOH), combination of sulfur proceeds more slowly, while the stage at which fresh latex is flocculated by an acid is reached only after a more prolonged period or, at a still higher pH value, is not reached at all. Also these observations agree with the other data, which indicate that, to reach the flocculation stage of fresh latex, the conditions of the reaction must be chosen so that as little hydrolysis as possible of the serum components occurs.

## COMBINATION OF SULFUR

It is evident from the experiments described above that, especially in a moist state, there are great differences between the mechanical properties of films obtained from vulcanized fresh latex and those obtained from vulcanized old or purified latex. To explain this phenomenon, it is necessary to discuss the various possible causes.

Fresh latex may differ from old latex in:

(1) the degree of polymerization of the rubber hydrocarbon;

(2) the extent to which hydrolysis of the serum components has taken place; and

(3) the content of free fat acids.

In this connection it may be noted that factors (1) and (2) go hand in hand. With reference to (1), it may be remembered that Spence and Ferry[11] indicated the likelihood that latex preserved with ammonia polymerizes on storage; on the other hand, however, Kemp and Peters[12] consider it probable that the opposite is the case, namely, that latex direct from the tree contains almost exclusively gel rubber. Leaving this question aside, we merely point out that there are actually certain indications in the literature with reference to possible differences in the behavior of rubber hydrocarbon itself. For this reason, we must first of all discuss the possibility that the phenomenon which we are endeavoring to explain results from differences in the way in which sulfur combines, which in turn may be caused by differences in the degree of polymerization of the rubber.

However, very little is known of the manner in which combination of sulfur takes place in the latex state.

Freundlich and Hauser[13], by means of microscopic observations and a micromanipulator, and Green[14], by microscopic observations in ultraviolet light, found evidence pointing to the probability that the rubber particles in vulcanized latex consist, to a great extent at least, of vulcanized rubber; Hauser and Bender[15] arrived at the same conclusion from other experiments. In view of

these publications, therefore, it is not likely that the vulcanized state depends solely on reaching the dry condition.

The writer would add still another factor, that, when determining, before and after vulcanization, the percentage of free sulfur in latex by Fowler's method, sulfur has actually been absorbed in the latex stage. This does not prove that this sulfur is actually combined with the rubber. If, however, vulcanized fresh latex is boiled with alkali and then is diluted and creamed in a centrifuge, the latex is highly purified with respect to its ash and nitrogen content, whereas its sulfur content cannot be reduced below the combined sulfur. Also the flocculate obtained by adding an acid to vulcanized fresh latex behaves in the same manner. It was found possible to reduce the nitrogen content to 0.014 per cent, but the sulfur content still was 1.4 per cent, this sulfur being present entirely in the form of combined sulfur. Only traces of free sulfur could be found. Through the mediation of the Rubber Foundation, finally, we had the privilege of becoming acquainted with the results of an analysis by Dekker[16] of a rubber powder prepared by us from vulcanized fresh latex. From the sample, Dekker prepared a rubber tetrabromide which was found to contain 1.1 per cent of sulfur (calculated on the basis of the original sample).

From all these data, therefore, it follows that the dry rubber obtained from vulcanized latex is composed chiefly of rubber that has combined with sulfur; with a degree of probability bordering on certainty that this same condition is present in vulcanized latex. This holds good for vulcanized fresh, old, or purified latex.

Nevertheless, the possibility remains that, in fresh latex, another form of combination of sulfur exists than in the case of old latex.

From the preceding remarks, it is evident that combination of sulfur during vulcanization does not differ essentially in fresh and in purified latex. Nevertheless this fact alone does not warrant the conclusion that the reactions proceed in the same way. It is probable, although no proof can be found in the literature, that, in the course of the vulcanization of latex, sulfur dissolves first; this dissolved sulfur then diffuses in the rubber, and only then is it possible for vulcanization to take place. The possibility must, therefore, not be excluded that the speed of combination of sulfur observed by us is merely dependent on the rate at which it diffused throughout the rubber, and that it is not necessarily characteristic of the reaction. To discover which is the slowest reaction, the following experiments were conducted.

Ammoniated latex was divided into two portions. The first portion was heated for 30 minutes with sulfur (2 grams per 100 grams of rubber); the other portion was heated similarly but without any substance having been added. After cooling, zinc oxide and Vulcafor-SDC were added to the first portion; to the second portion sulfur, zinc oxide, and Vulcafor-SDC were added. Both latices were then in part vulcanized in the latex state and in part were poured onto glass plates and vulcanized after drying at (1) room temperature, (2) 80° C, and (3) 120° C. These experiments were made with fresh ammoniated latex and with old purified latex. The results proved that, by preliminary heating with sulfur:

(1) vulcanization of latex is at first accelerated;
(2) dry vulcanization at room temperature is at first slightly accelerated;
(3) dry vulcanization at 80° and at 120° C is not noticeably accelerated.

The acceleration of vulcanization at 80° C is evident from Table 12, which gives data on the combined sulfur of vulcanizates from fresh latex.

TABLE 12

INFLUENCE ON THE VULCANIZATION OF LATEX AT 80° C OF PREHEATING
WITH SULFUR

| Time of vulcanization (min.) | Combined sulfur in % in TS rubber | |
|---|---|---|
| | Heated 30 min. at 80° C | Heated 30 min. at 80° C with sulfur |
| 0 | 0.00 | 0.02 |
| 10 | 0.04 | 0.41 |
| 20 | 0.61 | 0.91 |
| 30 | 0.64 | 0.99 |
| 60 | 0.93 | 1.23 |
| 120 | 1.48 | 1.69 |

In view of these results, the data on combined sulfur in Table 6 cannot be used for drawing conclusions as to the mechanism of the combination of sulfur. It should be noted further that, on preheating with sulfur, the sulfur which combines should not be regarded as comparable to that which takes place with rubber in fresh latex, because the effect of preheating must not be overlooked. From these experiments, therefore, one may conclude that if latex is heated at 80° C with dispersed sulfur in the presence of zinc oxide and an ultra-accelerator, solution of the sulfur is one of the factors which govern the combination of sulfur, both in fresh and in purified latex. No difference was observed in the behavior of fresh latex and old latex.

Furthermore it was ascertained how sulfur dissolves in the rubber of fresh latex and in that of old latex. After heating latex for 30 minutes at 80° C, it was diluted to a dry rubber content of approximately 7 per cent. It was then centrifuged for 20 minutes in a tube-centrifuge, creaming occurred in the tubes, and a serum layer was obtained having a dry rubber content of 4 per cent and a cream layer with a dry rubber content of 30–50 per cent. Undissolved sulfur settled at the bottom of the tube. Free sulfur was determined both in the cream and in the serum, in both cases on the basis of the dry substance. These two contents showed in various tests a difference that varied only within the limits of permissible error. From this it is concluded that the free sulfur content in the serum (in the dilution actually used) is negligible. In this way it was found that the rubber of purified old latex, after being heated 30 minutes with 2 parts of sulfur per 100 parts of rubber, had a sulfur content of 1.07 per cent, and that of fresh latex 1.03 per cent. In these experiments, the ammonia content of both latices was made identical, since the ammonia content probably affects not only the speed at which sulfur dissolves, but also the equilibrium ultimately attained between sulfur dissolved in the rubber and that in the serum. It must be remembered that, in the determination of the free sulfur, as applied by us according to the method of Fowler, the sulfide content is not included, and the polysulfide only in part. Thus sulfur could have been present in the serum, and even in the rubber, in a form that the analysis failed to detect.

Analogous tests, in which creaming was induced, not in tubes but in a De Laval separator, and in which the sulfur determinations were not made with the latex itself but with creped coagulum obtained after calcium chloride had been added, gave practically the same results.

It may be noted that, although the latex was heated with sulfur at 80° C, the results do not represent the conditions prevailing at that temperature, since centrifuging had to be resorted to. Thus the equilibrium that had been

attained possibly after about 30 minutes at 80° C was broken both by the drop in the temperature and by dilution of the latex. The data obtained are, therefore, more likely to refer to a state of equilibrium at about 30° than at 80° C. To eliminate the effect of heating, the sulfur was dissolved at room temperature. After 3 days, 0.90 per cent of the sulfur had dissolved in the rubber; after 14 days 1.04 per cent. Subsequently a gradual decline set in, possibly because some of the sulfur combined with the rubber. After 35 days, there was still 0.88 per cent of free sulfur in the rubber.

It may be noted here that the values obtained agree tolerably well with those obtained by Kelly and Ayers[17] with reference to the solution of sulfur in dry rubber. These investigators found that, at 30° C, 1.01 per cent sulfur dissolved in rubber. They proved also that the solubility of sulfur in rubber increases with increase in the vulcanization coefficient. Although no tests were made with reference to this, it is probable that this may be assumed to hold good for rubber in the latex state. This leads to the conclusion that it is not possible to remove by mechanical means all the free sulfur from vulcanized latex. Also after vulcanized latex has settled and has been decanted, or after it has been clarified in a centrifuge, it still contains free sulfur dissolved in the vulcanized rubber. That this free sulfur induces further vulcanization is certain, especially in view of the fact that, according to Mackay[18], accelerators also dissolve in rubber.

Although the experiments present a few new aspects of the problem, they do not lead to an explanation of the difference in the behavior of fresh latex and old (purified) latex during vulcanization. We may now turn to the question as to what extent the serum components of latex may be responsible for this difference.

## THE PART PLAYED BY THE ADSORPTION FILM ON THE LATEX PARTICLES

Hauser and Bender[15] proved that, when old latex is vulcanized, the surface tension of the mixture remains unchanged. This we were able to confirm for vulcanized fresh latex. It was found also that the addition of an ammoniacal dispersion of vulcanization ingredients to the serum of fresh latex does not result in any lower surface tension when the latex is heated for several hours at 80° C, than that obtained with fresh latex itself. It seems reasonably certain, then, that there is no adsorption replacement of the proteins surrounding the rubber particles during vulcanization[19].

But, by a different method, indications were obtained that the manner in which the proteins are adsorbed on the rubber particles of vulcanized fresh latex differs from that in ordinary latex. This view is based on experiments in which vulcanized fresh latex, in the stage at which a flocculate is formed by the addition of acid, was purified by repeated dilution and centrifuging in a De Laval separator. The effect of centrifuging was increased by supplying the artifice already referred to above, concerning which no further information can be given at this time. Before centrifuging, the latex or the latex mixture was diluted to a dry rubber content of about 5 per cent, was centrifuged to a dry rubber content of approximately 50 per cent, and was diluted again (to 1 part of cream 9 parts of water were added) if the centrifuging was to be repeated. Crepes were prepared by coagulating latex or cream, after dilution to a dry rubber content of about 5 per cent with formic acid. The results are set forth in Table 13. A single purification of the heated latex-ammonium

## TABLE 13

### REPEATED PURIFICATION BY PHYSICO-MECHANICAL MEANS; EFFECT ON THE COMPOSITION OF RUBBER OBTAINED FROM UNVULCANIZED LATEX MIXTURES

Latex 11; compound 3.
Data are in percentage of weight, for crepe and for whole-latex rubber.

Analyzed

| Composition of the mixture | Latex, not heated | Latex + casein | Latex + casein + zinc oxide | | Heated 2 hours at 80°C | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Latex + casein + SDC | Latex + casein + sulfur | Latex + casein + SDC + sulfur + zinc oxide | | |
| | Nitrogen | Nitrogen | Nitrogen | Zinc oxide | Nitrogen | Nitrogen | Nitrogen | Zinc oxide | Total sulfur |
| Mixture | 0,36 0,87 | 0,38 0,88 | * | | 0,40 0,80 | * | 0,41 0,78 | 0,84 1,54 | 1,79 1,86 |
| Heated mixture | | 0,56 0,85 | 0,54 0,82 | 0,03 1,20 | * | * | 0,62 0,79 | 0,31 0,56 | 1,63 1,78 |
| Diluted cream 1 | 0,09 0,10 | 0,07 0,08 | 0,19 0,23 | 0,02 0,12 | 0,13 0,13 | 0,10 0,12 | 0,23 0,24 | 0,13 0,21 | 1,49 1,57 |
| Diluted cream 2 | | | 0,04 0,03 | 0,03 0,02 | | | 0,12 0,12 | 0,05 0,13 | 1,44 1,56 |
| Diluted cream 3 | | | 0,02 0,04 | 0,02 0,02 | | | 0,08 0,09 | | |

\* Approximately identical with the data obtained for latex + casein.

casein left the nitrogen content at 0.07 per cent. When, during heating, Vulcafor-SDC or sulfur was present, the crepe obtained from the cream had a somewhat higher nitrogen content. When zinc oxide was present, the nitrogen content after purifying once was three times this percentage. This is a clear indication that this substance favors adsorption of nitrogenous compounds on the rubber. Vulcanized latex which has been purified only once retains a still higher nitrogen content. The purification was repeated with latex heated with zinc oxide, and with vulcanized latex. The results show that the nitrogenous components do not combine with the rubber, since they can subsequently be removed practically altogether by purely physical means. In vulcanized latex, the nitrogenous components are apparently a little more closely adsorbed to the rubber than they are in latex which is heated only with zinc oxide. By heating latex alone, a crepe was obtained that had a distinctly higher nitrogen content than that of crepe from latex that had not been heated. The changes in the proteins by heating seemed, however, to have practically no influence on the effect obtained by purification by merely physical methods.

It is not, therefore, heating latex as such, but heating in the presence of zinc compounds and even in a greater measure by vulcanization in the presence of zinc compounds, that results in an increased adsorption of the nitrogenous compounds on the rubber.

Table 13 gives the results with and without zinc content (expressed as zinc oxide). Here coagulation was effected by means of an acid, and as a result the crepes had lower zinc contents than whole-latex rubber. For this reason attention should be confined to the values for whole-latex rubber. In heating latex with zinc oxide, a small proportion of zinc seems in some way to be so tenaciously held by the rubber particles that it is not removed in the first purification. After the second purification, however, practically all zinc has been removed, so evidently it is not a question of chemical combination with some substance in the latex particle. The zinc has dissolved in the rubber, has been adsorbed on the rubber itself, or has been adsorbed on (or perhaps chemically combined with) some substance in the adsorption layer of the rubber particle.

The fact that the higher adsorption of zinc compounds goes hand in hand with a higher adsorption of nitrogenous compounds indicates that this last possibility is the correct explanation.

In view of this, it seemed desirable to investigate what differences there are in the quantities of zinc remaining adsorbed on the latex particles of different latices heated with zinc oxide or vulcanized, and purified by mechanical means. If the hypothesis is correct, then less zinc will be adsorbed by purified than by unpurified latex, provided the latices are manipulated in the same way, whereas less zinc remains adsorbed by an old latex than by a fresh one. The tests were carried out in the same manner as were the determinations of the quantities of sulfur dissolving within the latex particles.

After first heating the latex mixtures under controlled conditions with respect to their ammonia and their dry rubber contents, they were diluted to dry rubber contents of about 7 per cent. Each diluted mixture was centrifuged in a tube centrifuge, whereby the undissolved proportion of the added zinc oxide was precipitated to the bottom of the tube. The cream layer which formed in the tube was removed and desiccated at room temperature. The zinc content was determined in the rubber thus obtained. In the tests, the results of which are shown in Table 14, the latices were heated to 80° C for 1 hour, either with zinc oxide alone or as vulcanizing mixtures.

TABLE 14

ADSORPTION OF ZINC TO THE LATEX PARTICLES

Latex compound 2.

| Latex | Pretreatment | Latex stored | Zinc (as ZnO) in percentage of weight of the dried cream | |
|---|---|---|---|---|
| | | | Heated with ZnO 1 hour | Vulcanized 1 hour |
| A | creamed 4 times | 1½ years | 0.07 | . . . |
| B | centrifuged 2 times | ½ year | 0.11 | 0.14 |
| C | centrifuged once | 11 days | 0.13 | . . . |
| D | ammoniated field latex | fresh | 0.47 | . . . |
| E | ammoniated field latex | 1 day | 0.24 | 0.94 |
| E | ammoniated field latex | 8 days | 0.21 | 0.73 |
| E | ammoniated field latex | 1 month | 0.28 | 0.42 |

The results show that the quantity of zinc adsorbed on latex particles is closely related to the age of the latex and also, insofar as concentrated latices are concerned, to their degree of purification.

The difference in behavior, described in the preceding paragraphs, between vulcanized fresh latex and vulcanized purified latex can be explained, in view of these results, in the following manner. When fresh latex is vulcanized, a considerable quantity of zinc combines with the adsorption layer of the latex particle; this probably leads to isolation of the rubber itself, so that the films from such latex have but little tensile strength. When purified latex is vulcanized, much less zinc is adsorbed; hence the isolation is very considerably less.

The question then arises how the great difference between the zinc content of vulcanized fresh-latex particles and that of latex heated only with zinc oxide is to be explained. The data in Table 13 show that the zinc content of vulcanized latex can be greatly reduced (down to 0.13 per cent) by physico-mechanical means. It may be assumed that this remainder, not eliminated in this way, consists of zinc sulfide within the rubber itself. There is the further possibility that vulcanized latex contains zinc combined with accelerator; this latter zinc is probably present in the rubber, but it should be possible to remove it by "purification", i.e., by repeatedly washing the rubber. Although in Table 14 we referred to adsorbed zinc, it is almost certain that, in the case of vulcanized latex, not all the zinc is present in an adsorbed state.

Finally the following considerations may be put forward. In the dry vulcanization of rubber, it is well known that with most accelerators zinc oxide fulfils its function as an activator only in the presence of a sufficient quantity of higher fat acids. Now it is to be presumed that the adsorption of zinc on latex particles requires the presence of acid groups in the adsorption layer; so the question arises whether the slight adsorption of zinc in the case of purified latex is not to be accounted for by a lack of fat acids in the adsorption layer. On the basis of the literature, this question can be answered in the negative, since it is known that the fat acid content increases during storage of the latex. But there is also experimental proof that, by adding soap to old or purified latex, the course and the final state of vulcanization are not affected.

## DISCUSSION

It is conceded nowadays that vulcanized rubber consists of elongated rubber molecules twisting and coiling along and about one another, and chemically coupled by sulfur. By way of precaution the writer would remark that he

accepts this picture only provisionally and only for rubber that has been plasticized and vulcanized above 100° C. Under these conditions the latex globules, which in crude rubber probably occur mainly as individual units, have become merged. Rubber thus plasticized and vulcanized at a high temperature is likely to have a more or less homogeneous structure, and this is probably the structure of ordinary vulcanized rubber.

However, when vulcanized latex is dried at room temperature, rubber with a different structure results. Although each individual latex particle is normally vulcanized, it should not be assumed that, immediately on the formation of the film, primary bonds form between the rubber of the various latex particles. For this reason the structure of a rubber film obtained by drying vulcanized latex must be discontinuous; the forces which unite latex particles can only be secondary or van der Waals forces. The tensile strength of such a film is governed mainly by the magnitude of these secondary forces, and thus depends in a very large measure on the extent to which these particles in the film can approach one another. From these observations it is evident that films from vulcanized latex have a tensile strength which declines considerably as the relative humidity of the atmosphere increases, while at a given relative humidity the tensile strength is greater to the extent that the latex has been purified.

The effect of water may perhaps be ascribed in part to swelling of the adsorption film, which causes the particles to draw further apart. At the same time the water and other polarizable liquids screen off the dipolar activity of the various latex particles by virtue of their own polarization.

The representation of a film from vulcanized latex described above is accurate only if it is assumed that vulcanized rubber molecules behave at room temperature like the molecules of a solid, that is to say, if no transfer of any molecule from one latex particle to another latex particle takes place. Now it is possible that such transfer does take place in the case of latex particles with a very thin adsorption layer or that here and there are without such a layer. On the other hand this concept becomes less definite if, as a result of progressive vulcanization in the dry state, a sulfur bridge forms between rubber molecules pertaining to different latex particles. This latter possibility in particular may readily occur experimentally.

Under certain conditions the rubber particles in vulcanized fresh latex have a relatively thick adsorption layer, so the van der Waals forces are already a minimum in the dry state, while in a moist state films have practically no tensile strength. In the preceding discussion the conditions under which these conditions prevail have been explained, and it was shown also that the insulating layer surrounding these particles probably contained zinc. Evidently in this case the adsorption layer is so thick that contact between the rubber of one latex particle with that of another becomes impossible; therefore there is question of rubber particles running together and of sulfur bridges forming between rubber molecules of different latex particles. Vulcanized fresh latex, provided it has been vulcanized under the conditions discussed, has, when dried, an ideal discontinuous structure, whereas vulcanized old or purified latex assumes a structure which is a gradual transition to that of latex films dry-vulcanized at a low temperature.

This structural difference in films when dry and when moist, and the phenomena which manifest themselves on subsequent dry vulcanization of films from vulcanized latex are in harmony with this concept. In this respect it was always the tensile strength and the modulus of the films that guided our

considerations. In later studies, concerning which no report can yet be made, we shall investigate to what extent other properties, such as water diffusion, swelling, and permanent set, offer proof of structural differences. A more thorough discussion, which also will take into account the observations of other investigators on the structures of vulcanized and unvulcanized latex films, will be published after the new samples referred to above are available.

## SUMMARY

Patents granted to Schidrowitz[2] show that when latex is vulcanized and then dried at room temperature, the product has the properties of vulcanized rubber. Films produced in this way show tensile strengths and elasticity which correspond to those of latex films vulcanized in the dry state.

It is apparent, however, that when fresh latex is vulcanized under certain definite conditions, the product has fair tensile strength and elasticity only at a relative humidity of zero, but which under ordinary atmospheric conditions is brittle, seems to be overcured, and is practically without tensile strength. This tensile strength, however, is increased by additional dry vulcanization, so there can be no question of overcure. Just as soon as vulcanization has proceeded to a point where brittle films without tensile strength are obtained, the latex, when treated with acid, does not coagulate, but merely flocculates. Nor can such vulcanized fresh latex at this stage be made to coagulate coherently by other means. This form of latex is not sticky.

The flocculate referred to can be obtained only by vulcanizing fresh latex in the presence of zinc oxide, and under conditions such that hydrolysis of the nonrubber substances is a minimum. It is, therefore, desirable to have recourse to ultra-accelerators and to be sure that the vulcanization temperature is not too high. By keeping fresh latex alkaline, or by purifying it, it will not flocculate. Latex that has been purified or aged may occasionally, under similar conditions, give a brittle and incoherent coagulum, whereas in other cases a normally coherent but somewhat brittle coagulum results. The nature of the coagulum is governed by the degree of purification and hydrolysis of the nonrubber substances; hence all transition stages between a flocculate and a completely coherent coagulum may occur. By adding serum from fresh latex to purified latex, the behavior of such purified latex changes in the sense that it behaves more like fresh latex.

In studying experimentally the difference in behavior of fresh latex and purified latex, the first thing considered was the combination of sulfur. It was found that sulfur first dissolves in the serum, after which it dissolves in the rubber itself. Only then does vulcanization take place. This became evident from the definite acceleration of the combination of sulfur in the latex stage, when before vulcanization, latex was heated with sulfur alone. By this preparatory treatment too, dry vulcanization at room temperature was accelerated, but there was no noticeable effect on dry vulcanization at 80° and 110° C. At 30° C, about 1 per cent of the sulfur dissolved in the rubber particles, in the form of free sulfur. From this it was concluded that it is not possible to remove by mechanical means (as by clarification) excess free sulfur from vulcanized latex. No essential difference could be found between the combined sulfur of fresh latex and that of purified old latex.

The nonrubber substances are not combined chemically with the rubber by vulcanization in the latex stage, but they are adsorbed to a greater degree. This may be concluded from the experiments in which vulcanized latex was

purified by physico-mechanical means.    Mere heating of latex did not induce a higher adsorption of the components containing nitrogen; but heating with zinc oxide alone did induce such action.    In addition to components containing nitrogen, zinc was adsorbed by the rubber particles to a considerable extent. This makes it probable that during vulcanization a reaction sets in between the zinc-ammonia complex and the components containing nitrogen which are present in the adsorption layer of the latex particles.    It was found that under identical conditions fresh latex adsorbs much more zinc on its rubber particles than does purified latex.

In view of these results, the difference in behavior of fresh latex and of purified latex must be ascribed to differences in the thickness and the composition of the adsorption layers on the latex particles.    The rubber particles in fresh latex would, by vulcanization, become coated to such an extent that the mutual forces of attraction between the particles, on which the strength of the films depends, would be a minimum.    This is particularly so when the films are in a moist state, *i.e.*, when the adsorption layer is swollen.    On this basis, it must be assumed that there is a considerable difference in structure between plasticized, dry-vulcanized rubber and rubber from vulcanized latex, especially from vulcanized fresh latex.    Whereas in the former case one may assume that there is a continuous structure of long rubber molecules that twist over and along each other, and chemically bridged by sulfur linkages, in the latter case there is a discontinuous structure, consisting of latex particles which singly present a picture of normally vulcanized rubber held together, not by chemical bonds, but by van der Waals's forces.

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# IMPORTANCE OF ACIDIC COMPONENTS IN COMPOUNDING AMMONIA–PRESERVED LATEX WITH ZINC OXIDE *

## W. G. WREN

When concentrated, ammonia-preserved latex is kept in the presence of zinc oxide for some days, it often undergoes progressive thickening, thus giving rise to difficulties in many manufacturing processes, particularly those which employ dipping or extrusion. Although this difficulty can partly be avoided by selecting a "low Z.O.T." latex[1] or by chemical treatment[2], the factors which give rise to changes in viscosity are not completely understood. The investigations described below demonstrate the importance of naturally occurring acidic substances in compounding ammoniated latex with zinc oxide, and indicate that these substances have a marked effect on thickening. In the first section the solubility of zinc oxide in ammoniacal solutions and in latex serum is considered; in the second, the electrometric estimation of acidic substances, with a view to classifying latices; and in the third, the influence of acidic substances on the viscosity of latex compounded with zinc oxide.

## SOLUBILITY OF ZINC OXIDE IN LATEX

A consideration of the facts already known concerning the thickening of ammonia-preserved latex in the presence of zinc oxide leads to the view that the viscosity changes involve a chemical reaction, probably between zinc oxide and nonrubber serum substances; thus support of this theory is given by observations such as the progressive nature of the thickening, the reduction in viscosity changes after purification of latex by centrifuging[1], and the decrease in thickening when a suitable amount of caustic potash is added[2]. This view necessitates solution of the zinc as the first stage of the reaction, although the amount dissolved need be only small; attention was, therefore, first directed to an investigation of the solubility of zinc oxide in latex serum.

*Solubility of Zinc Oxide in Ammoniacal Solutions.*—Zinc oxide is only slightly soluble in ammonia, but the addition of ammonium salts markedly increases the amount dissolved, and it is, therefore, probable that if ammonium salts are present in ammoniated latex, appreciable quantities of zinc are dissolved, the amount depending on the strength of the ammonia, the nature and quantity of serum substances present, and possibly on the proportion of zinc oxide added[3]. An examination was therefore made of the effect on the solubility of zinc oxide in ammonia of various substances likely to be present in latex serum. The solutions were prepared by shaking, the excess zinc oxide being removed by centrifuging after a given time, and the zinc in solution estimated by precipitation as zinc ammonium phosphate, care being taken that any organic substances present were first destroyed by heating with concentrated sulfuric and nitric acids. The data are recorded in Table 1. Clear solutions were obtained in each experiment save those with oleic, linoleic and stearic acids and casein, in which cases the solutions appeared opaque and may

TABLE 1

INFLUENCE OF VARIOUS ADDED SUBSTANCES ON THE SOLUBILITY OF ZINC OXIDE IN
1.3 PER CENT AMMONIA SOLUTION

| Substance added to give $\frac{M}{20}$ solution | Zinc oxide dissolved (per cent) after: | | | | |
|---|---|---|---|---|---|
| | 1 hour | 1 day | 3 days | 7 days | 14 days |
| Nil | 0.03 | 0.05 | 0.05 | 0.05 | 0.05 |
| Hydrochloric acid | 0.20 | 0.22 | 0.22 | 0.20 | 0.23 |
| Phosphoric acid | 0.57 | 0.73 | 0.74 | 0.72 | 0.74 |
| Acetic acid | 0.31 | 0.23 | 0.24 | 0.36 | 0.23 |
| Caproic acid | 0.19 | 0.25 | 0.27 | 0.30 | 0.29 |
| Stearic acid | 0.11 | 0.05 | 0.05 | 0.08 | 0.09 |
| Oleic acid | 0.21 | 0.31 | 0.22 | 0.20 | 0.27 |
| Glutamic acid | 0.35 | 0.43 | 0.48 | ... | 0.51 |
| Aspartic acid | 0.43 | 0.46 | 0.45 | 0.48 | 0.45 |
| l-Tyrosine | 0.43 | 0.46 | 0.45 | 0.46 | 0.43 |
| Casein (commercial) 3 per cent | 0.36 | 0.38 | 0.34 | 0.39 | 0.39 |

have contained zinc in a colloidal condition; the solubilities in these cases are thus open to question. It will be seen that acid substances have a marked effect in increasing the solubility of zinc oxide. Thus 0.5 per cent phosphoric acid solution increases the solubility from 0.05 to 0.7 per cent in 1 per cent ammonia.

In the case of straight-chain carboxylic acids, the higher the molecular weight the lower is the solubility of the oxide, whereas with amino and mineral acids the amount dissolved appears to be approximately the same for equivalent amounts. Thus monobasic hydrochloric acid gives a value of about 0.2, glutamic and aspartic acids, which are dibasic, give 0.4 to 0.5, and tribasic phosphoric acid gives about 0.7. Experiments were also carried out, using 0.05 per cent ammonia solutions, but the values obtained were not reliable, as the amounts of zinc dissolved were very small; the results again indicated a marked increase in the solubility of zinc oxide in the presence of acid substances.

The increase in solubility is generally accounted for by the formation of a soluble zinc-ammonia complex salt which ionizes to give divalent ions, such as $Zn(NH_3)_3^{++}$ [4] or $Zn(NH_3)_4^{++}$ [5]. The complex salt appears to be formed chiefly in the presence of ammonium salts and, in accordance with this view, the removal of ammonium ions from solution by the addition of caustic potash was found to reduce the solubility of the zinc, thus:

| Caustic potash added to give pH value of | 8.5* | 9.0 | 10.0 | 11.0 | 12.0 |
|---|---|---|---|---|---|
| Amount of zinc oxide dissolved in 1.2 per cent ammonia solution, containing acetic acid | 0.111 | 0.109 | 0.098 | 0.065 | 0.022 |

* Initial pH, without added caustic potash.

The reduced solubility of zinc oxide in the presence of caustic potash may account for the phenomena of the KOH number method of Jordan[2], which demonstrates a progressive change in the properties of latex compounded with zinc oxide when increasing amounts of fixed alkali are added.

The amounts of protein and acids present in ammonia-preserved, field latex are generally comparable with the quantities used in Table 1, an M/20 solution corresponding to an acid value of about 400 mg. of caustic potash on a dried rubber film from 40 per cent latex. It is thus reasonable to suppose that similar quantities of zinc oxide would be taken up by latex serum containing

TABLE 2

SOLUBILITY OF ZINC OXIDE IN SERUM OF AMMONIATED LATEX

| Latex | Zinc oxide dissolved | | Ratio of amounts of serum solids present |
|---|---|---|---|
| | Per cent serum | Ratio | |
| Field latex | 0.29 | 1.5 | 2.7 |
| Centrifuged | 0.19 | 1.0 | 1.0 |
| Centrifuge skim | 0.48 | 2.5 | 5.1 |
| Creamed | 0.18 | 0.9 | 1.3 |

1.3 per cent ammonia (*i.e.*, 0.78 per cent on 40 per cent latex), and experiments have shown this to be the case. Table 2 shows the solubility of zinc oxide in sera prepared from a series of latices by creaming from a dry rubber content of 20 per cent, the ammonia content being subsequently adjusted to 1 per cent. The amounts of solids present in the sera are also given in the table, and will be seen to give a rough correlation with the amount of zinc oxide dissolved.

The next experiments were undertaken to determine whether the amount of zinc oxide dissolved in the serum had a direct influence on the viscosity of latex. An ammonia-preserved latex was treated with 0.1 per cent sodium pentachlorophenate (as a bactericide) and air-blown to remove excess ammonia until the pH value was reduced to 8.2. This treatment was carried out because it has been found that the viscosity changes occurring in latex containing zinc oxide are more pronounced at low ammonia contents. Part of this latex was creamed with sodium alginate to give a clear serum, which was then shaken with 1.5 per cent zinc oxide; the solubility of the latter was determined at intervals. To another part of the latex, 1.5 per cent zinc oxide was added, and the viscosity of the mixture determined at corresponding intervals, measurements on untreated latex also being made. The data obtained, recorded in Table 3, show that, although both the solubility of the zinc oxide and the

TABLE 3

VISCOSITY OF LATEX COMPARED WITH AMOUNT OF ZINC OXIDE DISSOLVED IN SERUM

| Period | Zinc oxide dissolved in serum (percentage) | Viscosity (seconds) | | Ratio |
|---|---|---|---|---|
| | | A Untreated latex | B Latex and zinc oxide | $\frac{B}{A}$ |
| 1 hour | 0.018 | 25.4 | 29.0 | 1.14 |
| 2 days | 0.032 | 26.3 | 30.3 | 1.15 |
| 4   " | 0.058 | 26.5 | 33.4 | 1.26 |
| 6   " | 0.054 | 24.0 | 33.0 | 1.38 |
| 10   " | 0.059 | 25.5 | 42.5 | 1.67 |
| 14   " | 0.044 | 32.0 | 54.0 | 1.69 |

viscosity increase on storage, there appears to be no direct correlation between them. Thus, although the experiments show that zinc oxide dissolves in ammoniated latex serum and causes thickening, the amount of zinc present in solution is not the only factor controlling viscosity. This was partly to be expected, as it was thought probable that thickening was due to adsorption of complex zinc ions from solution by the rubber globules. The amount of zinc associated with particles would then probably be the controlling factor in modifying the properties of the latex, and although the adsorption would depend on the presence of zinc in solution, other factors, such as the surface composition of the globules, would undoubtedly play an important part in determining the quantity of ions adsorbed. The next step in the investigation

was, therefore, an attempt to determine whether the rubber globules actually adsorb zinc from solution, and what part is played in the thickening process by substances at the rubber-water interface.

*Distribution of Zinc Oxide in Latex.*—To determine whether zinc oxide dissolved in latex is present entirely in the serum or whether it becomes associated with the latex globules, experiments were carried out in which latex containing zinc oxide in solution was separated into cream and serum; by estimating the zinc in both fractions, the amount associated with the rubber



PERMEABLE MEMBRANE
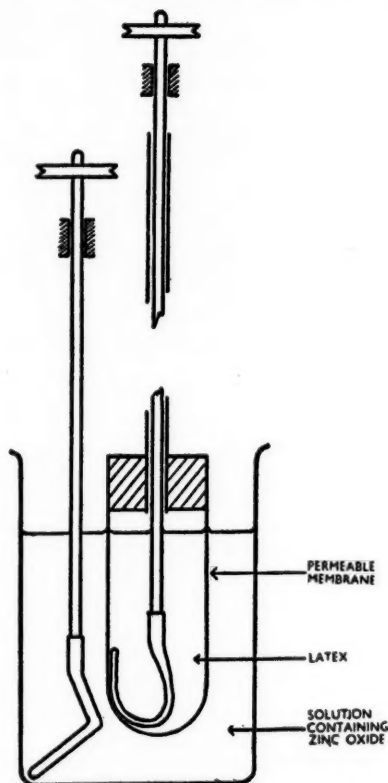
LATEX

SOLUTION CONTAINING ZINC OXIDE

FIG. 1.—Apparatus for diffusion of zinc-ammonia ions into latex.

phase could be calculated.    In the first attempts, ammoniated latex was shaken with zinc oxide and the excess separated by centrifuging; complete removal of undissolved zinc oxide by this means, however, was found to be impracticable.    To avoid the presence of solid zinc oxide, a solution of the latter in ammonia and ammonium phosphate was then added to latex, but since the solubility was not high, the concentration of zinc finally obtained in the latex was rather low, unless a large amount of the ammonium salt was added. Further experiments were therefore carried out, in which latex, contained in a collodion membrane of large-pore size, was immersed in a suspension of zinc oxide, either in ammoniated serum or in a solution of 1 per cent ammonia and 1 per cent ammonium phosphate.    By this means a continual supply of

zinc complex ions passed into the latex, and contact with solid zinc oxide was avoided.   The latex in the collodion sack was gently stirred by a flexible rubber tube, which scraped cream from the walls as soon as it was formed; the outer suspensions of zinc oxide were also gently agitated (see Figure 1).   After about 20 hours the latex was removed, well mixed, a sample removed and the rest allowed to cream after the addition of sodium alginate (Manucol V); the zinc present in the serum and in the creamed concentrate was then determined. The method of estimation was to destroy the organic substances with nitric acid, followed by boiling with a few millilitres of concentrated sulfuric acid until water-clear.   This solution was diluted to about 200 cc., and rendered alkaline by the addition of ammonia, followed by ammonium phosphate, and heated just to boiling; any precipitate of iron, etc., was filtered off and washed with ammonia solution.   The filtrate and washes were then gently heated on the water-bath to expel ammonia, whereupon the zinc precipitated in good crystalline condition; it was filtered off on a fine sintered glass crucible, washed with ammonium phosphate solution, cold water and finally 50 per cent alcohol, dried, and weighed as zinc ammonium phosphate.

From the data obtained, the amount of zinc associated with the rubber phase was calculated; typical values are shown in Table 4.   Owing to experi-

TABLE 4

DISTRIBUTION OF ZINC OXIDE IN AMMONIATED FIELD LATEX

| Conditions of experiment | | Zinc oxide present (percentage) | | |
| --- | --- | --- | --- | --- |
| Dialysis | Fractionation | In serum | In con- centrate | Asso- ciated with rubber |
| 1. 20 hours against:<br>  1.0 per cent $NH_3$<br>  0.5 per cent $(NH_4)_2HPO_4$<br>  2.0 per cent ZnO | By creaming | 0.5 | 0.3 | 0.15 |
| 2. 20 hours against serum containing:<br>  0.5 per cent $NH_3$<br>  4.0 per cent ZnO | "        " | 0.3 | 0.3 | 0.2 |
| 3. 24 hours against:<br>  1.0 per cent $NH_3$<br>  1.0 $(NH_4)_2HPO_4$<br>  2.0 per cent ZnO | By centrifuging | 0.35 | 0.2 | 0.2 |

mental difficulties in estimating accurately such small proportions of zinc in rubber, the values must be regarded as a rough estimate, but they demonstrate quite definitely that, after passing into solution in the serum, zinc is in part removed from the aqueous phase, and becomes associated with the rubber globules.   This may be explained by the adsorption of positively-charged complex zinc ions by negatively-charged latex globules, possibly leading to the formation of insoluble compounds with surface-active materials situated at the rubber-water interface.   It has been suggested by Wren[6] that the surface of the rubber globule consists either of a monolayer of mixed fat acids and pro- tein, or of a duplex layer with the protein outermost, and it is thus possible that insoluble zinc proteinate and zinc soaps are formed.   Evidence showing the possibility of this explanation was obtained from a series of experiments, carried out with the collodion membranes previously mentioned, in which com- plex zinc ions were allowed to pass into a solution of various substances in dilute ammonia.   The result of this work may be summarized as follows:

| | Outside membrane | | Inside membrane | | Observations |
|---|---|---|---|---|---|
| 1 | $NH_3$<br>$NH_4Cl$<br>ZnO | 0.05 per cent<br>1.0 " "<br>5.0 " " | $NH_3$<br>Oleic acid | 0.05 per cent<br>1.0 " " | Precipitate containing Zn and oleic acid |
| 2 | $NH_3$<br>$NH_4Cl$<br>ZnO | 0.35 per cent<br>1.0 " "<br>5.0 " " | $NH_3$<br>Oleic acid | 0.35 per cent<br>1.0 " " | Precipitate |
| 3 | $NH_3$<br>ZnO | 0.05 per cent<br>5.0 " " | $NH_3$<br>Oleic acid | 0.05 per cent<br>1.0 " " | No precipitate |
| 4 | $NH_3$<br>$NH_4Cl$<br>ZnO<br>Casein | 0.05 per cent<br>1.0 " "<br>5.0 " "<br>1.0 " " | $NH_3$<br>Oleic acid | 0.05 per cent<br>1.0 " " | Precipitate |
| 5 | $NH_3$<br>$NH_4Cl$<br>ZnO | 0.05 per cent<br>1.0 " "<br>5.0 " " | $NH_3$<br>Oleic acid<br>Casein | 0.05 per cent<br>1.0 " "<br>1.0 " " | White opalescence which tended to settle out |
| 6 | | do. | $NH_3$<br>Linoleic acid | 0.05 per cent<br>0.1 " " | Precipitate |
| 7 | | do. | $NH_3$<br>Stearic acid | 0.05 per cent<br>0.1 " " | Precipitate |
| 8 | | do. | $NH_3$<br>Aspartic acid | 0.05 per cent<br>0.1 " " | No precipitate |
| 9 | | do. | $NH_3$<br>$l$-Tyrosine | 0.05 per cent<br>0.2 " " | No precipitate |
| 10 | | do. | $NH_3$<br>Casein | 0.05 per cent<br>1.0 " " | White opalescence which tended to settle out |
| 11 | | do. | Serum from field latex by creaming | | Precipitate |
| 12 | $NH_3$<br>Linoleic<br>  acid<br>ZnO | 0.05 per cent<br><br>0.1 " "<br>5.0 " " | $NH_3$<br>Linoleic acid | 0.05 per cent<br>0.1 " " | Precipitate |

The first two experiments demonstrate that zinc oxide passed into solution in the presence of ammonium salts, and ammonia and was then precipitated by oleic acid; the precipitate formed quite slowly and continued to increase for some days. Experiment 1 represents the conditions of precipitation of zinc by fat acids associated with the latex globules at a low pH value of about 9.5. Experiment 3 shows that no precipitate is formed unless an ammonium salt (or its equivalent) is present to enable zinc to pass into solution. The presence of protein, either in the outer or in the inner compartment, does not affect the formation of insoluble zinc oleate but, in the latter case, appears to peptize it to some extent (Experiments 4 and 5). Of the other substances tried, it was found that the amino acids, aspartic acid and $l$-tyrosine, gave no precipitate, whereas linoleic acid, stearic acid, casein and serum from a field latex gave insoluble zinc compounds. It is thus apparent that the higher fat acids and protein appear to precipitate the zinc, whereas amino acids and, of course, lower fat acids have no effect.

Briefly summarizing this section, the conclusions drawn are: (1) that mineral, amino, long- and short-chain carboxylic acids and casein have a marked

effect in increasing the solubility of zinc oxide in ammoniacal solution. The solubility of zinc oxide in latex serum has been shown to depend to some extent on the amount of serum substances present, (2) that when zinc oxide dissolves in latex, part of the zinc becomes associated with the rubber globules, and (3) that the formation of insoluble compounds is possible from the reactions of zinc ammonia complex ions with protein and higher fat acids, such as may be present at the rubber–water interface, or in the serum of ammonia-preserved latex.

## ELECTROMETRIC TITRATION OF LATEX

The investigations already carried out indicate that the acidic substances in ammoniated latex (present as ammonium salts) probably play a major role in controlling the solubility of zinc oxide in the serum, and the next step taken was an attempt to confirm this indication. To do this, it was necessary to determine the acids naturally present in latex, and the method adopted was electrometric titration, using a glass electrode.

The obvious method was to titrate the acid with alkali, in a manner similar to that used in determining the KOH number of latex, which, it is claimed, "is a measure of the titrable acidic constituents in latex"[2]. In this method, the ammonia content of the latex is reduced to 0.2 per cent by the addition of formaldehyde to give a sharper end-point. This treatment has been criticized by Schrieke[7], who has shown that the addition of formaldehyde may vitiate the titration. Apart from this criticism, the direct titration of acidic substances in latex with fixed alkali is not entirely straightforward, owing to the presence of protein hydrolysis products, particularly amino acids[8] which, owing to their nature, undergo deionization of the amino $-NH_2^+$ group, and not ionization of the $-COOH$ group, as in normal carboxylic acid titration with alkali. As it is desired to determine the acidic components in latex, a correct value will be obtained by fixed alkali titration only if amino and carboxylic groups are present in equivalent amounts; according to Whitby and Greenberg[8], however, monoamino dicarboxylic acids, such as aspartic acid, are naturally present in latex serum, so that equivalent amounts of amino and carboxylic groups are probably not present. Thus, to estimate the carboxylic groups of aminoacids, titration with an acid is necessary, so that they may become deionized by an equivalent amount of strong acid. Titration of ammoniated latex with acid does, however, estimate free ammonia and other basic substances present, and also includes back-titration of ammonium salts of weak acids. An examination of the theoretical basis of the titration of latex was, therefore, undertaken in an attempt to clarify the position before carrying out practical determination with alkali and acid.

### Theoretical Considerations

*Titration with caustic potash.*—The electrometric titration of ammoniated latex with caustic alkali gives a curve with a point of inflection at pH 11 to 11.5. This point of inflection is accounted for by the fact that the natural curve is composed of two curves, A and B, as shown in Figure 2, A corresponding to the change in pH brought about by the addition of alkali to the volume of water present, B corresponding to the actual titration of the acid-reacting substances present in the latex. The correct titration values are therefore obtained from the experimental curve by subtracting curve A, thus giving curve B. When this is done, the corrected latex-alkali titration curve

is found to approach the vertical at about pH 11.5, indicating that only a small amount of untitrated material is left at this pH (see Figure 5). It is not to be expected that the corrected curve would become absolutely vertical at pH 11 to 12 (*i.e.*, that there are no more titrable substances present), for, although the acidic substances would probably be completely dissociated at this stage, except extremely weak acids, some basic groups in proteins and
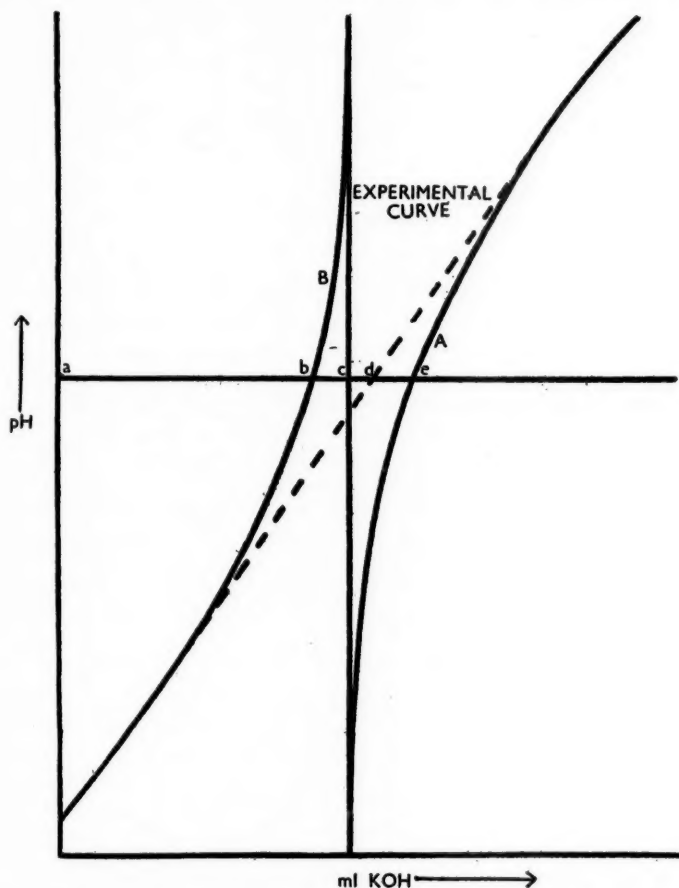


Fig. 2.—Theoretical titre of acidic substance at a given pH = *ab*. Titre of alkali to raise pH solution to that value = *ce*. Addition of *ce* to *ab* = *ad* = curve, as determined experimentally.

amino acids are still untitrated, according to the reaction for zwitterions:

$$NH_3^+ \cdot R \cdot COO^- + OH^- \rightarrow NH_2 \cdot R \cdot COO^- + H_2O$$

These groups, guanidine and $\epsilon$-amino, occur in arginine and lysine, which, according to Tristram[10] and Whitby and Greenberg[8], are present in protein from rubber latex. Thus, taking the end-point at pH 11 to 11.5, the values obtained actually represent a titre of acidic substances, such as mineral acids and carboxylic acids, together with protein and amino acids radicles which

dissociate in this region, *viz.*, iminazole, $\alpha$-amino, hydroxy, $\epsilon$-amino and, possibly, guanidine. Of these, the acids with a pH value up to 9 to 10 and the iminazole and $\alpha$-amino groups, which have pH values of about 6 and 9.5, respectively, are probably estimated in their entirety, the others only in part. The acids are probably combined with ammonia and back titrate with caustic potash, thus:

$$HA + NH_3 \rightarrow A^- + NH_4^+$$
$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$
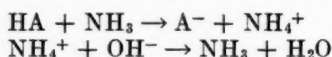
In a similar manner any reaction between amino groups and ammonia would also be back-titrated with caustic potash, thus:

$$NH_3^+ \cdot R \cdot COO^- + NH_3 \rightarrow NH_2 \cdot R \cdot COO^- + NH_4^+$$
$$NH_4^+ + OH^- \qquad \rightarrow NH_3 + H_2O$$
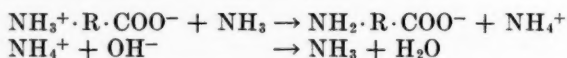
The other protein groups, hydroxy, $\epsilon$-amino and guanidine, have pH values of about 10, 10.5 and 12.5, respectively, which, in the case of the two weaker bases, is equal to the pH value at the half-titration point; thus, assuming a dissociation range of about 4 pH units, these will be estimated only in part if the end-point is taken at pH 11 to 11.5. Little, if any, of the strongly basic guanidine group is titrated, as it dissociates at a higher pH and over a smaller range. In the presence of formaldehyde, however, the basicity of the amino and guanidine groups is reduced[11], and it is possible that more of the $\epsilon$-amino and guanidine groups would then be titrated. It is thus apparent that the titration of latex to the end-point used in the KOH number test does not yield a definite quantity, but is an estimate of the acidic substances and the less basic groups of proteins and protein breakdown products.

*Titration with hydrochloric acid.*—In titrating ammoniated latex with hydrochloric acid, the titre from the alkaline region to pH 7 is largely taken up by ionization of ammonia. Back-titration of the ammonium salts of very weak acids, such as the higher fat acids and the dissociation of amino groups of proteins and protein breakdown products, will also be included, thus:

$$NH_2 \cdot R \cdot COO^- + H^+ \rightarrow NH_3^+ \cdot R \cdot COO^-$$
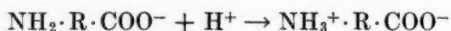
It will, therefore, be appreciated that the estimation of ammonia by titrating latex with an acid to an indicator end-point, such as that given by bromothymol blue or methyl red, is not likely to yield an accurate value; the more serum substances there are present the greater will be the error due to buffering. Experiment has shown that a difference of 10 per cent can occur between the titres given by the indicators mentioned. The more protein and protein breakdown products there are present, the greater is this difference likely to be; in fact, the latter may be taken as a measure of the amount of buffering substances present. Most of the ammonia will be dissociated at pH 7, however, and from that value to the end-point (at pH 1 to 2), the acid titre is a measure of part of the iminazole groups (pK 6) and of $\alpha$ and $\beta$ (or $\gamma$) carboxyl groups, which have pK values of about 2.0 and 4.0, respectively, and titrate thus:

$$NH_3^+ \cdot R \cdot COO^- + H^+ \rightarrow NH_3^+ \cdot R \cdot COOH$$
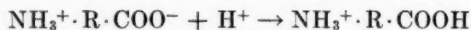
Also ammonium salts of weak acids, such as acetic acid, are back titrated in this region, but very weak acids, such as oleic, will not be included. When the pH value drops below pH 3, correction for the amount of acid required to reduce the pH of the water present becomes appreciable, and the curve must

be corrected in a manner similar to that mentioned in the case of caustic potash titration.    The end-point can be chosen at an arbitrary pH value (*e.g.*, 1.5) or may be taken where the corrected curve becomes approximately vertical. The titre from pH 7 to the end-point then includes part of the iminazole groups, the $\alpha$ and $\beta$ (or $\gamma$) carboxyl groups and most of the weak acids with pK values from about 2 to 6.    By taking the titre from pH 6 to the end-point, less of the iminazole groups is included, but less of the weaker acids is estimated.

## TITRATION OF LATEX

*With caustic potash.*—Preliminary experiments were carried out to demonstrate the estimation of acids by titrating to pH 11–11.5 with caustic potash in the presence of ammonia.    Figure 3 shows the curve obtained by titrating
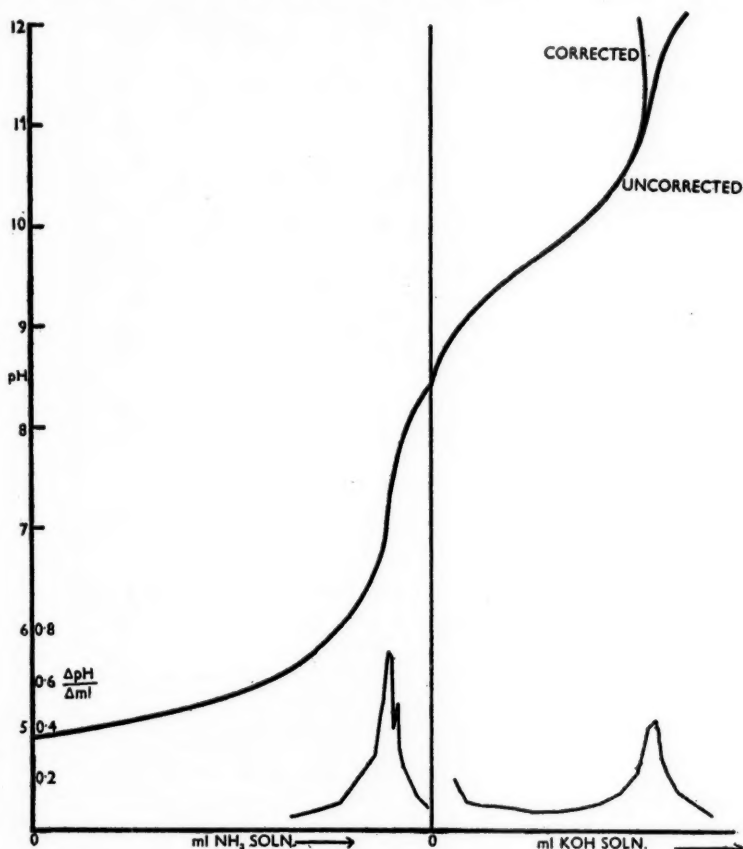


FIG. 3.—Titration of acetic acid first with ammonia, then with caustic potash.

acetic acid in the presence of ammonia; it is seen to be very similar in shape to that obtained in the KOH number titration of latex.    The corrected titre of caustic potash up to the end-point, taken where the curve becomes vertical,

was found to agree with the amount of acetic acid taken, within the limits of experimental error; thus, in the experiment shown in Figure 3, the acetic acid added was equivalent to 8.9 cc. of $N$ solution and the corrected caustic potash titre to the end-point was 8.8 cc.; the uncorrected value being 9.2 cc. Further experiments demonstrating the part played by ammonia in the KOH number titration were carried out with a 40 per cent field latex preserved with sodium pentachlorophenate and containing no ammonia; the titration curves are shown in Figure 4, from which it will be seen that no point of inflection at pH 11 to
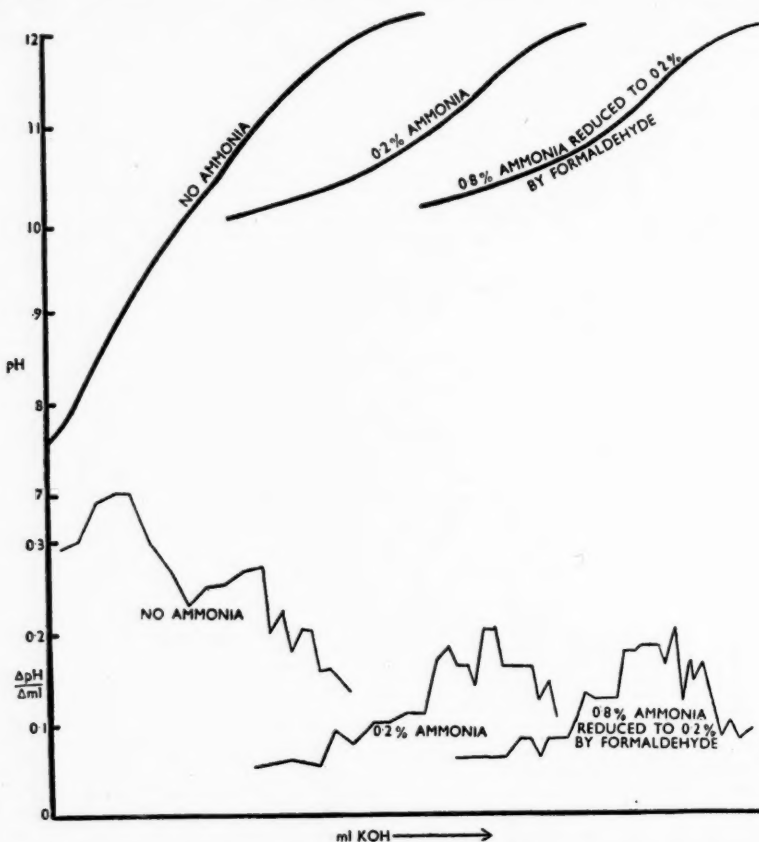


FIG. 4.—Caustic potash titration of field latex preserved with sodium pentachorophenate, before and after addition of ammonia.

11.5 was found until ammonia was added. This experiment clearly indicates that the end-point at this pH is the completion of the reaction:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$
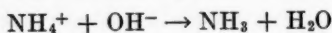
and that a measure of the acids present is obtained by determining the amount of $NH_4^+$ ions produced from the reaction of the acid with an equivalent amount of ammonia, thus:

$$HA + NH_3 \rightarrow NH_4^+ + A^-$$
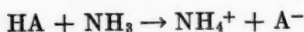
Determination of the KOH number curves of a series of latices was then carried out after the method of Jordan[2]. The results are shown in Figure 5, with the corrected curves. It is interesting to note that the slope of the corrected curves at the end-point decreases as the amount of serum substances present increases from latex 1 to latex 5. The diagrams also show $\Delta pH/\Delta ml.$ plotted against the titre. It will be seen from the latter that it was often
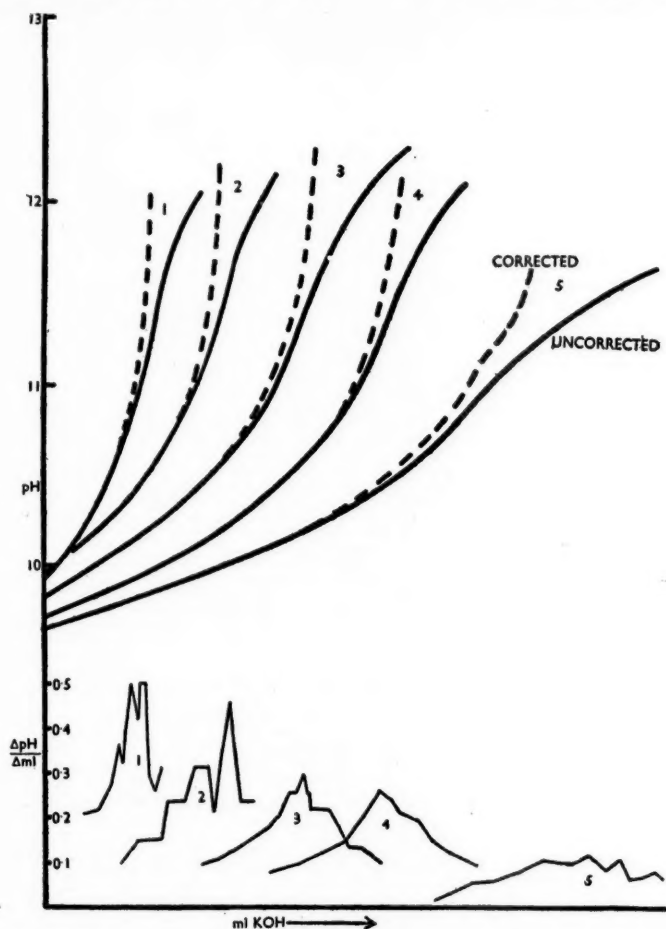


Fig. 5.—Caustic potash titration of a series of latices containing increasing amounts of serum substances, from 1 to 5.

difficult to decide the position of the point of inflection, and the KOH numbers are in consequence somewhat indeterminate; the values obtained are recorded in Table 5, which also gives the corrected values taken at pH 11.2. It will be seen that, although there is an appreciable difference in most cases, the correction does not generally amount to more than about ±2 per cent, which is not a serious difference for most purposes, as the values must of necessity be approximate. It is, therefore, probable that, to determine the "KOH num-

TABLE 5

Acids in latex expressed as cc. of N-solution per 100 g. of total solids

| Latex | KOH titration | | | HCl titration | | | | |
| | Direct | Corrected | Back-titration | Direct, corrected | | After adding KOH, corrected | | |
| | | | | From pH 7 | From pH 6 | From pH 7 | From pH 6 | |
|---|---|---|---|---|---|---|---|---|
| Field (4) | 23.3 | 23.8 | 20.3 | 21.5 | 15.7 | 20.8 | 15.1 | |
| Centrifuged concentrate (1) | 11.4 | 11.1 | 12.0 | 5.1 | 3.1 | 10.4 | 7.2 | |
| Centrifuged skim (5) | 48.3 | 48.1 | 45.7 | 33.2 | 28.7 | 52.3 | 40.5 | |
| Centrifuged skim, creamed (3) | 17.6 | 17.2 | 18.2 | 11.8 | 8.1 | 16.9 | 12.3 | |
| Creamed concentrate (2) | 15.3 | 15.2 | 15.3 | 12.0 | 12.7 | 14.9 | 10.3 | |

TABLE 6

Acid present per 100 g. of serum (cc. N-solution)

| Latex | KOH titre | | | | | | HCl titre | | | | Alcohol extraction | | ZnO dissolved per 100 g. serum after 24 hours (g.) |
| | Direct | | Corrected | | Back-titration | | From pH 7 | | From pH 6 | | Water soluble | Total | |
| | Serum | Latex | Serum | Latex | Serum | Latex | Serum | Latex | Serum | Latex | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Field | 16.49 | 16.51 | 15.33 | 16.72 | 14.85 | … | 17.9 | … | 15.49 | … | … | … | 0.530 |
| | 10.40 | 10.77 | 10.46 | 10.90 | 9.95 | 9.35 | 14.12 | 8.58 | 12.54 | 6.24 | 3.04 | 4.61 | 0.381 |
| | 10.22 | 11.03 | 9.02 | 11.08 | 8.96 | 10.36 | 12.35 | 10.13 | 10.73 | 7.65 | 2.64 | 4.59 | 0.335 |
| | 10.63 | 11.57 | 11.24 | 11.24 | 11.40 | 12.35 | 12.82 | 10.20 | 10.13 | 7.20 | 2.74 | 4.47 | 0.576 |
| Centrifuge concentrate | 7.5 | 4.98 | 7.16 | 4.87 | 6.55 | 5.28 | 8.93 | 6.49 | 7.17 | 4.48 | 1.17 | 2.31 | 0.291 |
| | 6.65 | 6.86 | 6.53 | 7.26 | 6.65 | … | 7.01 | … | 4.48 | … | 2.89 | 3.60 | 0.235 |
| | 3.76 | … | 2.57 | … | 2.90 | … | 4.29 | … | 3.47 | … | 1.26 | 2.08 | 0.128 |
| Centrifuge skim | 15.2 | 14.42 | 15.12 | 14.37 | 14.92 | 13.66 | 18.64 | 13.61 | 15.38 | 10.52 | 4.03 | 5.60 | 0.544 |
| Correlation coefficient, r | 0.99 | 0.85 | 0.99 | 0.87 | 0.99 | 0.80 | 0.99 | 0.87 | 0.96 | 0.88 | 0.75 | 0.86 | |
| Significant values of r* (P=0.05) for number of results taken | 0.63 | 0.67 | 0.63 | 0.66 | 0.63 | 0.76 | 0.63 | 0.76 | 0.63 | 0.76 | 0.67 | 0.67 | |

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ber", titration of the latex directly to a fixed pH, say, about 11, would be a simpler and more rapid method than the rather laborious determination of the titration curve and point of inflection, and would yield values at least as satisfactory. This method would also have the advantage that the same range of substances would then always be estimated, which is not the case when the end-point is taken at the point of inflection, as the latter occurs at different pH values, and is not actually the end of the titration.

*With hydrochloric acid.*—The curves obtained by titrating the series of latices mentioned above with hydrochloric acid are shown in Figure 6, and the
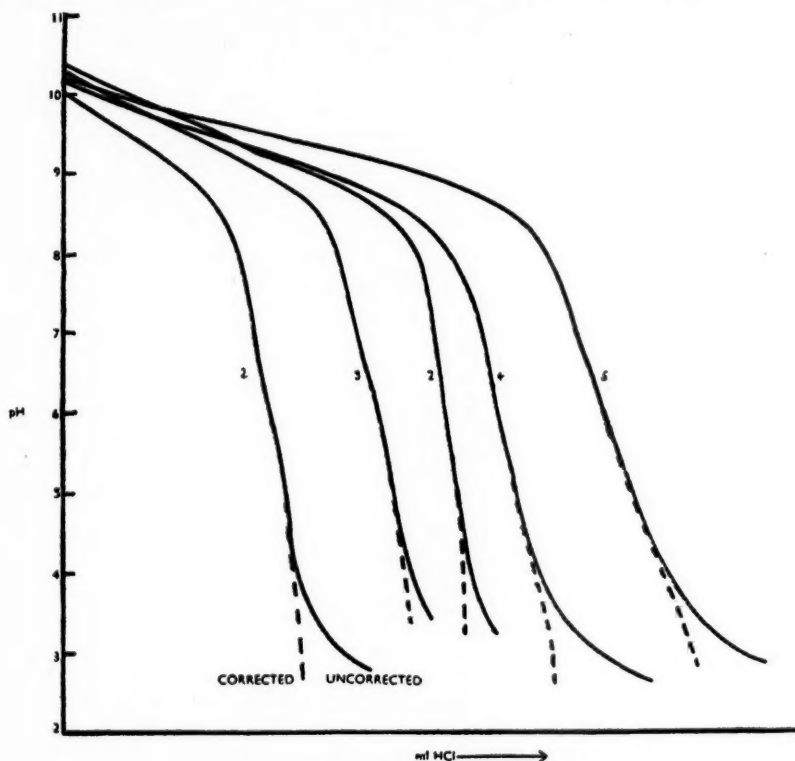


FIG. 6.—Hydrochloric acid titration of a series of latices.

values of the corrected titre from pH 7 and pH 6 to the end-point are given in Table 5. It will be noted that the curves show two points of inflection, *viz.*, at pH 7 and 5, which appear to merge one into the other; the significance of these points is discussed below. The figures for the acid titre are definitely lower than those by titration with caustic potash, and the titre from pH 6 is much smaller than that from pH 7. Further experiments were then carried out on the same latices, in which the pH value was increased to 12 by the addition of caustic potash, the latex then being titrated with hydrochloric acid, thus giving curves from pH 12 to pH 2, which are shown in Figure 7. It is seen that there is one point of inflection about pH 11 and two others at pH 7 and 5, merging one into the other.

To assist in explaining these curves, a solution containing known amounts of ammonia, acetic acid and caustic potash at pH 12 was titrated with hydrochloric acid; the curve obtained is shown in Figure 8 and indicates that the titre from 12 to the first point of inflection at pH 11 is equivalent to the caustic potash added in excess of that combined with the acetic acid; thus the acetic acid is measured by the amount of potash added, 8.5 cc. of $N$ solution less the back-titration and correction at pH 11, 1.0 cc., the value obtained, $8.5 - 1.0 = 7.5$ cc., being approximately equal to the amount of acetic acid originally added, 7.6 cc. The titre from pH 11 to the next point of inflection about 7,
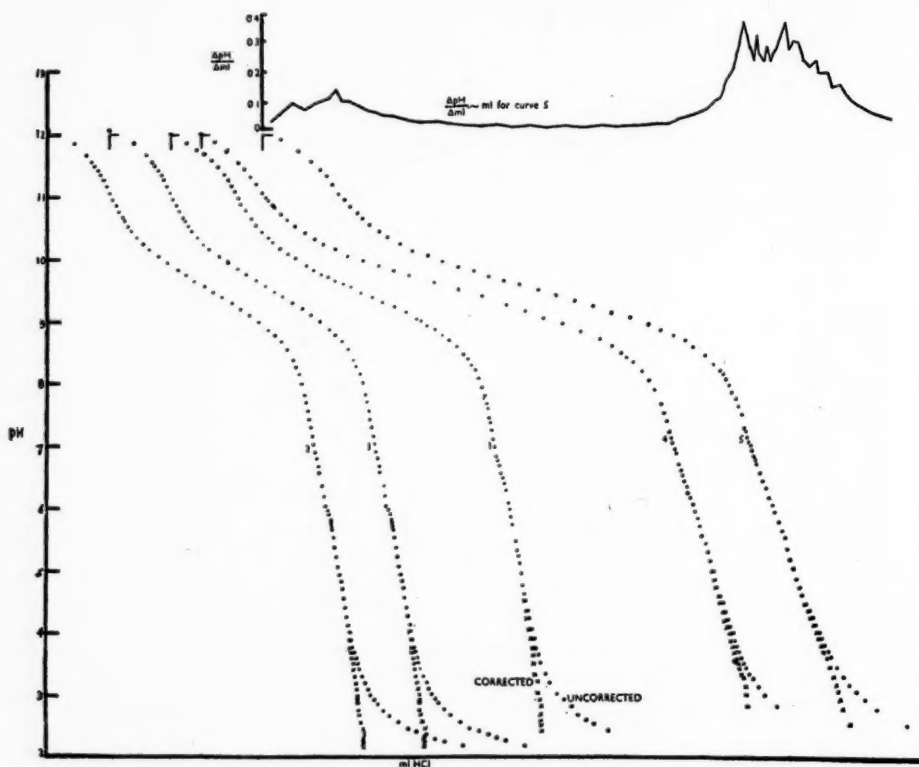


Fig. 7.—Hydrochloric acid titration of a series of latices, after adding caustic potash to pH 12.

9.3 cc., represents the amount of ammonia present in the solution, and is slightly less than the ammonia originally added (10.0 cc.), due to the loss of ammonia from the titration vessel after adding the caustic potash. From pH 7 to the last point of inflection, which after correction shows the curve to be almost vertical at the end-point, the titre is again equivalent to the acid present, and is approximately equal to the acetic acid originally taken, 7.3 cc., measured compared with 7.6 cc. taken. The discrepancy is probably due to the rather large corrections which have to be applied at this pH, in this case as high as 2.3 cc.

From the latex curves in Figure 7, it will now be seen that a measure of the acidic substances can be obtained from the amount of caustic potash added, less the back-titration to the point of inflection at pH 11, applying a correction, as in the case of the direct alkali titration. The figures obtained by this method, shown in Table 5, agree reasonably well with the direct titration, although in some cases a difference of 10 per cent was observed.

The point of inflection at pH 7 corresponds to the end-point of the ammonia titration, and the titre from this point to the end gives a measure of the acidic substances present (including part of the iminazole groups, as previously mentioned). From the pK value at the half-titration point of the titre between the points of inflection at pH 7 and 5 (approximately 6.5), it is thought that the latter point of inflection may be due to the carbon dioxide present; similar inflections at pH 7 and 5 have been reproduced in titrating caustic potash and
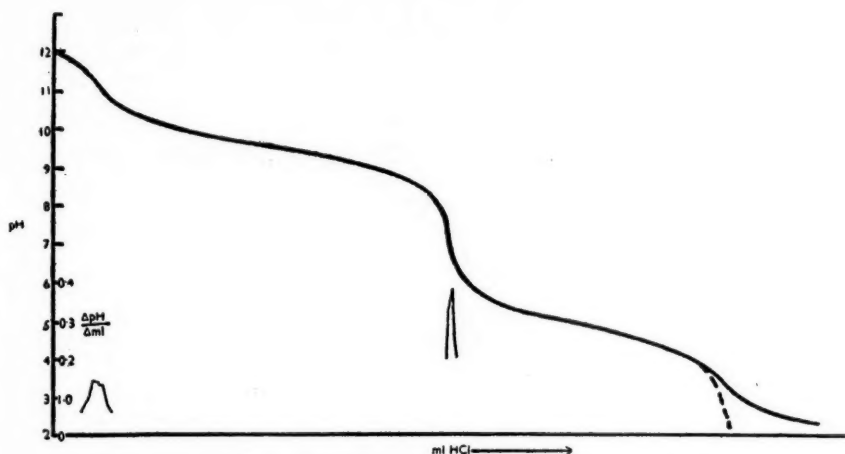


Fig. 8.—Hydrochloric acid titration of solution containing acetic acid, ammonia and caustic potash at pH 12.

ammonia containing a small amount of carbon dioxide, with hydrochloric acid. The corrected acid titres from pH 7 and pH 6 to the end-point are shown in Table 5, and agree with the caustic potash titre much better than the acid titres carried out directly on the latex without adding caustic potash; it will be seen that the titre from pH 7 gives closer agreement than that from pH 6.

From these results it appears that similar values for the acidic substances in latex are obtained by titration with caustic potash to pH 11, by the addition of excess fixed alkali and back-titration with acid to pH 11, and by titration with acid from pH 7 to the end-point in the presence of excess caustic potash. Of these methods, that which is most convenient for the purpose in hand would naturally be selected but, for general purposes, titration to a fixed pH about 11 to 11.5 with caustic potash or from pH 7 to about pH 2 with hydrochloric acid in the presence of fixed alkali appear to be the simplest and quickest methods. Preliminary experiments have shown that simple titration with caustic potash in the presence of an indicator (B.D.H. "11–13") giving a color change at pH 11 to 11.5 also gives approximate values, and thus eliminates the complication of the electrometric method.

It is of interest to note that titration of latices preserved with sodium
pentachlorophenate yields quite a different type of curve from that given by
ammoniated latex.   A typical curve is shown in Figure 9.   Latex preserved
with sodium pentachlorophenate, and containing no ammonia, shows three


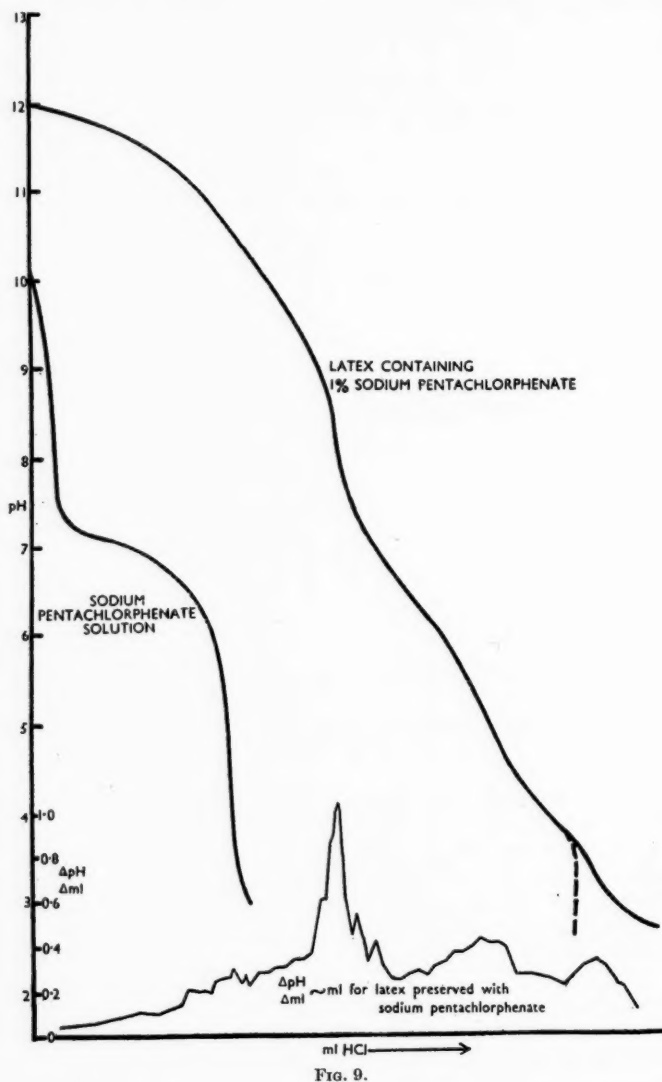
FIG. 9.

points of inflection; at pH 8, 4.5 and 3.   After correction, the inflection at
pH 3 is seen to correspond approximately with the end of the titration.   The
points of inflection at 8 and 4.5 correspond to those obtained by titrating
sodium pentachlorophenate containing a little free alkali with hydrochloric
acid, as shown in Figure 9.   To estimate the acids naturally present, one of

the following methods may, therefore, be adopted. The first method is to add ammonia and titrate with caustic soda to pH 11. This procedure does not give an accurate value, owing to the presence of free fixed alkali in commercial sodium pentachlorophenate. The amount of free alkali present can usually be estimated, however, and a suitable correction made. The second method is to titrate with acid from pH 8 to the end-point, which estimates the acidic substances present, including the pentachlorophenol; if the amount of the latter is known, a correction may then be made. This method overestimates the acidic substances present, as more of the amino groups of protein and amino acids are titrated than in titrating from pH 7. Alternatively, an approximate estimate of the acids present other than pentachlorophenol may be obtained by titrating from pH 6 to the end-point, as little of the pentachlorophenol remains undissociated at pH 6, as will be seen from the titration curve in Figure 9.

*Correlation of amount of zinc dissolved with acids present.*—Experiments were next carried out to show the relation between the proportion of the acid substances present in latex, and the solubility of zinc oxide. A series of eight different latices was taken and sera prepared from them by creaming from 30 per cent dry rubber content. The solubility of zinc oxide in the sera was then determined, and the acids present were estimated both by titrating the latices and by titrating the sera. Table 6 shows the resulting data. To compare the proportion of zinc oxide dissolved with the proportion of acids present, the results were treated statistically and the correlation coefficient between solubility and the proportion of acid present, determined by various methods, was calculated. It will be seen that the data obtained by titration of the sera gave a highly significant correlation, whereas the values obtained by titration of the latices show a distinctly lower correlation, which in some cases is only just significant. This difference may be accounted for by the fact that acidic substances associated with the latex globules would be titrated in the latex but would not be present in the separated serum and would, therefore, not influence the solubility of the zinc oxide. Values are also given for the acids, determined by alcoholic extraction of dried latex films by Baker[12]. Although the amount of total acids thus extracted is much lower than the amount estimated by electrometric titration of the latex, the values give a significant correlation comparable with that given by the latex titration figures. The water-soluble portion of the total acid extracted gives a definitely lower coefficient, but the correlation is still significant.

This section may be summarized briefly as follows. (1) The acid components in latex can be estimated only approximately by titration, owing to the presence of protein and products of protein hydrolysis. (2) Titration with caustic potash to a fixed pH, say at 11, or titration with hydrochloric acid in the presence of caustic potash from pH 7 to the end-point both appear to yield reasonable estimates of the acidic substances present, provided the experimental titre is corrected. (3) There is excellent correlation between the amount of acidic substances naturally present in latex serum, as estimated by electrometric titration, and the amount of zinc oxide dissolved by the serum, in a series of eight latices examined.

## THE INFLUENCE OF ACIDIC SUBSTANCES ON THE VISCOSITY OF COMPOUNDED LATEX

The experiments demonstrate the importance of naturally occurring acidic substances in controlling the solubility of zinc oxide in ammoniated latex, and

show that there is no direct correlation between the amount of zinc oxide dissolved and the thickening produced in latex, although the presence of zinc in solution is obviously necessary. Experiments also indicate that insoluble zinc compounds may be formed from the reaction of zinc-ammonia ions with proteins and higher fat acids, and it is thought possible that this is the process which gives rise to thickening, zinc being slowly precipitated from the serum, then replaced by more zinc oxide passing into solution, and so on.

The next stage of the investigation was to attempt to learn more about the processes involved in the thickening of latex by zinc oxide, and comprised a study of the changes in viscosity brought about by various substances, particularly acids. From investigations already described, it was predicted that the addition of ammonium salts, such as the chloride or acetate, should markedly increase the thickening of latex in the presence of zinc oxide, whereas the removal of electrolytes, particularly ammonium salts, should reduce the thickening. The following experiments confirm this deduction, and demonstrate the marked effect of ammonium salts of all acidic substances tried on the viscosity of ammoniated latex, after compounding with zinc oxide.

*Viscosity determination.*—A method of estimating the tendency of latex to thicken in the presence of zinc oxide has been described by Murphy[1]. It comprises measuring the time in seconds taken for 50 cc. of latex to flow through a standard orifice, 24 hours after mixing with 5 per cent of zinc oxide, the latex having been previously treated with formaldehyde to reduce the ammonia content to 0.05 per cent.

A similar method has been used in the present experiments, measurements having been taken at different time intervals. In the original method, latex with 59 per cent dry rubber content was used, and it was stated that although a dry rubber content of 34 per cent could be used, it was not generally so satisfactory as the higher value. The present experiments have confirmed this observation. Thus, a series of latices of varying dry rubber content, prepared by adding the required amount of serum to a field latex concentrated by creaming, showed that there was little difference between the Z.O.T. numbers of latex at 30 and 35 per cent dry rubber content, whereas at 40 and 45 per cent, the values showed a progressive increase (see Table 7). Further obser-

TABLE 7

EFFECT OF DRY RUBBER CONTENT ON VISCOSITY OF FIELD LATEX AFTER COMPOUNDING WITH 5 PER CENT ZINC OXIDE

| Dry rubber content | Viscosity (sec.) after: | | | |
|---|---|---|---|---|
| | 1 day | 2 days | 4 days | 14 days |
| 30 | 23 | 22 | 21 | 23 |
| 35 | 24 | 25 | 24 | 23 |
| 40 | 31 | 31 | 29 | 31 |
| 45 | 37 | 35 | 32 | 36 |

vations showed that marked differences at 59 per cent were inappreciable at 30 per cent, thus:

Z.O.T. VALUES

| | 59% | 30% |
|---|---|---|
| Latex A | 64 | 16 |
| Latex B | Too thick to measure | 17 |

In view of this, higher concentrations have been employed in the present series of experiments and, consequently, the field has been narrowed to concentrated latices.

*Effect of various acids on the thickening of ammoniated latex in the presence of zinc oxide.*—A centrifuged latex with a medium Z.O.T. value of about 60 was chosen for the experiments, in which the effect on the viscosity of added substances was observed after compounding with zinc oxide. Table 8 shows

TABLE 8

EFFECT OF VARIOUS ACIDS ON THE VISCOSITY OF CENTRIFUGED LATEX IN THE
PRESENCE OF ZINC OXIDE

| Acid added as ammonium salt | | Viscosity (sec.) after: | | | |
|---|---|---|---|---|---|
| | | 1 hour | 1 day | 3 days | 7 days |
| Nil | | 76 | 84 | 89 | 95 |
| Hydrochloric acid | 0.05 per cent | 96 | 124 | 135 | 171 |
| | 0.15 " " | 147 | 424 | 365 | coagulated |
| | 0.25 " " | 125 | 203* | 262* | 419* |
| Glutamic acid | 0.05 per cent | 94 | 102 | 110 | 110 |
| | 0.15 " " | 97 | 187 | 152 | 156 |
| | 0.25 " " | 102 | 215 | 300 | 312 |
| Acetic acid | 0.05 per cent | 94 | 109 | 110 | 116 |
| | 0.15 " " | 89 | 103 | 108 | 130 |
| | 0.25 " " | 109 | 232 | 268 | coagulated |
| Linoleic acid | 0.5 per cent | 74 | 98 | 102 | 103 |
| | 1.0 " " | 114 | 182 | 185 | 191 |
| | 1.5 " " | 145 | 610 | . . . | 690 |
| Stearic acid | 0.5 per cent | 89 | 65 | 67 | 77 |
| | 1.0 " " | 106 | 103 | 106 | 137 |
| | 1.5 " " | 147 | 108 | 120 | 154 |

\* Large clots formed.

the viscosity of the original latex at different time intervals, and after the addition of various acidic substances, in most cases added as a solution of the ammonium salt or soap. Increasing quantities of these acids produce increasing thickening in the latex; thus mineral acids, amino acids and carboxylic acids, including long-chain fat acids, are all active in this respect. The effect of the acids appears to be additive; thus the data given in Table 9 show that

TABLE 9

ADDITIVE EFFECT OF TWO ACIDS IN INCREASING THE VISCOSITY OF CENTRIFUGED
LATEX IN THE PRESENCE OF ZINC OXIDE

| Substances added | | Viscosity (sec.) after: | | | |
|---|---|---|---|---|---|
| | | 5 min. | 1 day | 3 days | 7 days |
| Nil | | 64 | 73 | 80 | 91 |
| Oleic acid 0.4 per cent | | 78 | 71 | 84 | 176 |
| " " 1.0 " " | | 92 | 126 | 284 | coagulated |
| NH₄Cl 0.2 " " | | 75 | 240 | 265 | coagulated |
| | | (64) | (55) | (61) | (61) |
| {Oleic acid 0.4 " " | | 373 | 336 | Very thick | coagulated |
| {NH₄Cl 0.2 " " | | (61) | (56) | (59) | (59) |
| {Oleic acid 1.0 " " | | >1000 | coagulated | . . . | . . . |
| {NH₄Cl 0.2 " " | | (110) | (67) | (73) | (74) |

(Figures in brackets are controls, of same composition but without zinc oxide.)

the addition of ammonium chloride and oleic acid both increase the viscosity change in latex when added together. As many of these acids occur naturally in ammonia-preserved latex as ammonium salts, it may be concluded that they

play a major role in controlling the thickening of latex in the presence of zinc oxide. Further evidence was obtained by observations on latex purified by dialysis, preliminary experiments indicating that the removal of electrolytes considerably reduces thickening occurring in the presence of zinc oxide. Considering now the mechanism of thickening, it was thought possible that the formation of zinc soaps, such as zinc oleate, might be responsible, owing to their tendency to invert an oil-in-water type of emulsion. The addition of 1 per cent of zinc oleate to latex showed, however, that thickening occurred only in the presence of moderately large amounts of ammonia. Thus thickening was observed in ammoniacal latex at pH 10.4, but no thickening at pH 9 (ammonia = 0.05 per cent), or when the pH value of this solution was increased to 10.4 by the addition of caustic potash (see Table 10). There is thus a

TABLE 10

EFFECT OF ZINC OLEATE ON VISCOSITY OF CENTRIFUGED LATEX

| Conditions | Amount of zinc oleate added (per cent) | Viscosity (sec.) after: | | | | |
|---|---|---|---|---|---|---|
| | | 10 min. | 1 hour | 1 day | 3 days | 7 days |
| pH of latex containing ammonia = 10.4 | 0.1 | 49 | 45 | 45 | 42 | 42 |
| | 1.0 | 75 | 120 | >1000 | very thick | .. |
| pH of latex containing ammonia (0.05 per cent) approx. 9 | 0.1 | 45 | 43 | 42 | 43 | 43 |
| | 1.0 | 54 | 54 | 53 | 53 | 53 |
| pH of latex containing ammonia 0.05 per cent + caustic potash pH 10.4 | 0.1 | 42 | 40 | 38 | 38 | 38 |
| | 1.0 | 45 | 46 | 43 | 44 | .. |

difference in behavior between zinc oleate added to the latex and that formed *in situ*. This may be accounted for by the difference in solubility of zinc oleate and oleic acid at pH 9. Thus, oleic acid passes into solution, and is probably adsorbed at the rubber–water interface, where it reacts with zinc–ammonia ions to form insoluble zinc oleate, as shown in the experiments with collodion membranes already described. In the case of zinc oleate, little passes into solution at pH 9, so the latex is not appreciably affected; in the presence of more ammonia, however, it passes into solution and probably becomes associated with the rubber globules, thus giving rise to the thickening observed at pH 10.4.

In view of the experiments carried out, it is suggested that the thickening of latex in the presence of zinc oxide comprises two processes, firstly, the adsorption of divalent zinc-ammonia ions by the negatively charged latex globules, with consequent lowering of the $\zeta$-potential and of the mobility of the particles and, secondly, the formation of hydrophobic zinc compounds at the rubber–water interface, thus causing desolvation of the globules and greater instability of the latex.

If desolvation of the globules is prevented by adding to latex an anionic soap which does not form an insoluble zinc compound, no thickening is observed after compounding with zinc oxide. It may be pointed out, however, that the addition of anionic soaps is not of great value in those technical processes which rely on ultimate coagulation of the latex, since these stabilizing agents render coagulation difficult and generally give rise to a weak coagulum. It is of interest that the addition of pentachlorophenol (prepared from Santobrite, commercial sodium pentachlorophenate, by the addition of hydrochloric

TABLE 11

EFFECT OF PENTACHLOROPHENOL ON THICKENING OF ZINC OXIDE-
COMPOUNDED LATEX

| | Time after mixing: | | | | | |
|---|---|---|---|---|---|---|
| | 5 min. | 1 hour | 1 day | 3 days | 7 days | 14 days |
| Control | 72 | 170 | 290 | 490 | coagulated | |
| +0.5 per cent pentachloro-phenol | 62 | 72 | 86 | 93 | 117 | 125 |

acid and extraction with ether) to a "high Z.O.T." ammoniated latex also markedly reduces thickening in the presence of zinc oxide, as shown in Table 11, which shows the viscosities at different time intervals of this latex after adding 3.0 per cent of zinc oxide with and without the addition of 0.5 per cent of pentachlorophenol, the pH value in both cases being adjusted to 8.8 by adding formaldehyde. Sodium pentachlorophenate was found to have a similar effect.

Summarizing this section, it is shown that the addition of ammonium salts of mineral, amino, and carboxylic acids markedly increases the viscosity changes which occur in latex after compounding with zinc oxide, and that the effect of the acids is additive. Evidence is given that the thickening in latex normally depends on the salts of naturally occurring acids. It is suggested that the thickening of latex by zinc oxide is brought about by the adsorption of zinc-ammonia ions to form hydrophobic zinc compounds at the surface of the latex globules.

### GENERAL CONCLUSIONS

In view of the experimental work described above, it appears that changes in viscosity of zinc oxide-compounded latex are due largely to the presence of ammonium salts of naturally occurring acids. These salts enable zinc to pass into solution, and to be absorbed by the latex globules, thus giving rise to the thickening commonly experienced. The amount of zinc passing into solution is directly proportional to the amount of acid present, and it is therefore suggested that determination of the acids by either of the methods described (viz., titration to pH 11 with caustic alkali, or from pH 7 to the end-point with hydrochloric acid), would form a sound basis for the classification of latices in regard to their behavior on compounding with zinc oxide. The investigations thus indicate that the variability of latex is due, in part at least, to the presence of acidic substances and may, therefore, be controlled by preventing the formation of the acids, or by their removal.

*Summary.*—It is demonstrated that naturally occurring acidic substances control the solubility of zinc oxide in ammonia-preserved latex, and it is concluded that they are probably the controlling factor in determining the increase in viscosity which occurs in latex compounded with zinc oxide. In support of this view, it has been shown that the addition of various types of acid to ammonia-preserved latex markedly increases thickening after mixing with zinc oxide, and that the removal of naturally occurring acids reduces the thickening. It is suggested that titration of the acids in latex by the methods described forms a sound basis for the classification of latices in regard to their behavior on compounding with zinc oxide.

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# DISTRIBUTION OF NON–RUBBER SUBSTANCES IN PRESERVED LATEX

## PART II.  ACIDS *

### H. C. BAKER

In a previous paper by the present author[1], a general method for determining the distribution of the nonrubber substances between the rubber-and-water phases in latex was described and results were given of its application to the study of the distribution of nitrogen and materials extractable with acetone.   It was shown that the nitrogen associated with the rubber phase is of two different types, a small amount (about 0.02 per cent) being independent of particle size and consequently distributed throughout the mass of the rubber, whereas the remainder is a function of particle size, replaceable by surface-active materials, such as soaps, and is, consequently, situated at the surface of the particles.

The surface nitrogen in ammoniated latex was variable, decreased with age of latex, could be partially desorbed at an alkaline pH by washing the latex, for instance, by dilution or repeated creaming, and is considered to represent the protective protein covering of the latex globules.   The total variation experienced in unconcentrated ammoniated latices of varying ages was from 0.11 to 0.18 per cent, but in latex of good quality about six months old, surface nitrogen was 0.15 per cent, corresponding to about 1 per cent protein.   Distribution experiments on the acetone extract showed that there is from 2 to 3 per cent of acetone-soluble substances associated with the rubber, of which less than one-half represents ammonium soaps at the surface of the particles.   The surface of the rubber particles is, therefore, composed largely of protein and fat acids, and it was thought probable that the ratio between them might change, both during the life of a single latex and from one latex to another.

Information about the nitrogen content of freshly preserved latex has been given by McGavack[2], who showed that nitrogen was inversely proportional to total solids over a range from 23 to 46 per cent of total solids, and that the total variation in nitrogen content was about 20 per cent.   These results suggest that the change is mainly in serum nitrogen, and that surface nitrogen is probably fairly constant in fresh latex.   If this is the case, variations in surface nitrogen occurring in ammoniated latex are due to the differing total effects of the factors influencing the hydrolysis of protein under alkaline conditions, e.g., the age of the latex, its degree of ammoniation, and the average temperature of storage.   It is of interest to note in this connection that surface nitrogen in nearly neutral latex preserved with 1 per cent sodium pentachlorophenate was 0.18 per cent.   This suggests that the low value of 0.11 per cent found by McGavack for freshly preserved latex soon after tapping may be due to small differences in technique, e.g., boiling the dried latex film with dilute alkali before determining of nitrogen by the Kjeldahl method.

Further work on the distribution of nonrubber substances in latex has now been directed towards a more detailed study of the acids removed from the

dried film by extraction with alcohol, which was found to be more effective than acetone. The alcohol extract was separated into two fractions, respectively soluble and insoluble in ether, the former being found to contain long-chain fat acids and esters, while the ether-insoluble portion contained the remainder of the free acids, which were water-soluble. Experiments on ammonia-preserved latex showed that the acids present are distributed as follows: (1) a large and markedly variable quantity of water-soluble acids in the form of ammonium salts in the water phase; (2) nearly 1 per cent of long-chain acids at the surface of the rubber particle, present as ammonium soaps. There is no evidence of marked variation except, of course, that centrifuged creams contain less than whole latex and much less than skim on account of differences in particle size, and (3) over 1 per cent of miscellaneous acids dispersed in the rubber phase, and occurring chiefly as esters. These are fairly constant when expressed as a proportion of the rubber phase in different latices.

Latices preserved entirely with sodium pentachlorophenate were found to exhibit striking differences from ammonia-preserved latices, in the high content of esters dissolved in the rubber and the almost complete absence of water-soluble acids in the aqueous phase. Latices preserved with sodium pentachlorophenate and 0.1 per cent ammonia showed a normal ester value and about one-half the quantity of water-soluble acids contained in the control latices preserved with ammonia only.

These results are considered to be of considerable technical importance because they indicate that esters and soaps are fairly constant for any given type of latex, and that there is an enormous variation in the amount of water-soluble acids (ammonium salts) in the aqueous phase. Taken in conjunction with Wren's findings that water-soluble acids control the solubility of zinc oxide in ammonia-preserved latex, leading to the adsorption of zinc by the rubber globules and thickening of the latex, it appears that the variation in water-soluble acids is a factor which is responsible for much variation in the behavior of compounded and deammoniated latex.

As a result of the experience gained in this investigation, it is considered that the determination of water-soluble acids is an important test for the quality of latex.

The above represents the broad conclusions reached, and these will be amplified and illustrated by experimental data in the sections which follow.

*Distribution of the acids in ammonia-presevred latex.*—Mention has already been made of previous experiments[1] on the acetone-extract of dried latex films. As a result of these experiments, it was tentatively concluded that over one-half of the acids in ammonia-preserved latex are water-soluble, but experience since has proved that extraction of dried films with alcohol is more reliable than with acetone, and separates more water-soluble acids, and a technique of examination of the alcohol-extract has been devised which separates it on the one hand into materials soluble in ether and, on the other, into materials soluble in water. Briefly, one portion of the hot alcohol-extract is examined for total acids by titration with alcoholic potash to a phenolphthalein end-point and, if the weight of the extract is desired, alcohol is removed and the neutralized extract is dried at 90° C, allowance being made for the potash added. The alcohol is removed from a further portion without titration, the cold extract is treated with ether, and the readily soluble fraction containing fat acids and esters is decanted and examined separately for free acids in the same way as the whole extract, and then for its ester value by saponification with alcoholic potash. If it is desired to know the amount of the ether-soluble

fraction, the ether extract is dried at 90° C and weighed, before carrying out the determination of free acids.   The remainder of the alcohol extract is almost entirely soluble in water, but is not used for the determination of water-soluble acids because of the irregular results obtained, these acids being determined by difference between total and ether-soluble acids.

A detailed description of the technique, an example of the calculation of distribution values, and the results of a chemical analysis of the alcohol extract are given as appendices to this paper.

A comparison of the acetone and alcohol extracts of a dried latex film examined by the above method is given in Table 1, which shows that the

### TABLE 1

#### COMPARISON OF ACETONE AND ALCOHOL EXTRACTS

| Nature of material | Extracted by acetone (per cent total solids) | Extracted by alcohol (per cent total solids) |
|---|---|---|
| Extract (g.) | 5.9 | 9.2 |
| Ether-soluble fraction of extract (g.) | 2.6 | 2.6 |
| Total acid value (mg. KOH) | 460 | 560 |
| Acid value of ether-soluble fraction (mg. KOH) | 240 | 225 |
| Water-soluble acid value (by difference) (mg. KOH) | 220 | 335 |

ether-soluble fraction of the extract is the same within the limits of experimental error, but that alcohol extracts considerably more water-soluble acids than acetone.

Table 2 shows how the alcohol-soluble substances and the corresponding ether-soluble substances are distributed between rubber and water in the original latex diluted to 20 per cent dry rubber content (see Appendix A).

### TABLE 2

#### DISTRIBUTION OF ALCOHOL-SOLUBLE SUBSTANCES IN LATEX

| Nature of material | Associated with rubber (per cent rubber) | Associated with water (per cent water) |
|---|---|---|
| Alcohol extract (g.) | 2.52 | 1.96 |
| Ether-soluble fraction of alcohol extract (g.) | 2.35 | 0.12 |
| Acids in alcohol extract (mg. KOH) | 174 | 112 |
| Acids in ether-soluble fraction of alcohol extract (mg. KOH) | 173 | 19 |

The outstanding feature of these results is that the whole of the acids associated with the rubber phase in latex are soluble in ether and that 95 per cent of the substances and 85 per cent of the acids in the water phase are insoluble in ether.   It is broadly true, therefore, that the ether-soluble substances are associated with the rubber phase, and the water-soluble substances with the aqueous phase.   The nature of the acidic components is dealt with further in Appendix C, in which it is indicated that the ether-soluble acids are chiefly long-chain fat acids, present in latex as soaps, and that the water-soluble acids are partly degraded protein and hydrolysis products of esters of water-soluble acids.

Although the results in Table 2 show that the ether-soluble acids are associated with the rubber phase, they do not indicate whether they are situated at the surface or are dispersed throughout the mass of the rubber particles.

The fact that they are likely to be present as ammonium soaps with surface-active properties is a strong indication that some at least are on the surface of the particle.    In this connection it may be pointed out that it was previously shown, from distribution experiments, that a portion of the nitrogen in latex was associated with the rubber phase, and that all except 0.02 per cent (calculated on the rubber) could be replaced by soap[1].    This replaceable nitrogen is clearly situated at the surface of the particle.    Confirmation of this is provided by the larger amount of nitrogen associated with the small particles in centrifuge skim, compared with that associated with the large particles in cream. Assuming that surface concentration is independent of particle size, it was calculated that the particles in the cream had a mean diameter approximately 2.5 times that of the particles in skim.    These results are shown again in Table 3, together with the corresponding figures for ether-soluble substances.

TABLE 3

DISTRIBUTION OF ALCOHOL-SOLUBLE SUBSTANCES IN DIFFERENT FRACTIONS OF THE SAME LATEX

|  | Parent latex | Centrifuged concentrate | Centrifuged skim | Creamed concentrate |
|---|---|---|---|---|
| Total solids (per cent latex) | 41.2 | 62.6 | 26.0 | 57.7 |
| Ester value of ether-soluble fraction (mg. KOH per 100 g. rubber) | 182 | 187 | 235 | 180 |
| Acid value of ether-soluble fraction (mg. KOH per 100 g. rubber) | 252 | 152 | 378 | 205 |
| Mean particle size ratio by acids | 1.50 | 2.49 | 1.00 | 1.82 |
| Mean particle size ratio by nitrogen | 1.54 | 2.56 | 1.00 | 1.75 |

There is a remarkably close agreement between relative mean diameters, calculated from the ether-soluble acids and the nitrogen associated with the rubber particle, indicating that the whole of these acids are at the surface and are not dispersed or dissolved in the mass of the rubber.    These relative mean diameters are also in agreement with values found by Wren[3] for a similar series of latices by determining the area occupied by monoparticle films spread on an aqueous surface.

Table 3 shows also that the ether-soluble esters form a fixed proportion of the rubber, except for the centrifuge skim and are, therefore, mostly contained within the rubber phase.

Hydrolyzable substances yielding acidic components are also present in the water phase, and it is of interest to consider the total potential development of acidic components from substances in the rubber and water phases in comparison with that found to have occurred at the time of examination of the samples.    Some typical results are given in Table 4, from which it will be seen that there is little scope for the further development of ether-soluble acids, but that a considerable amount of water-soluble acids may be developed if hydrolysis continues on storage of latex in the presence of ammonia.    An interesting feature of the results is that the bulk of the ether-soluble esters in the rubber phase give rise to water-soluble acids which are likely to pass into the water phase.

## SUMMARY

It may be concluded from the results of the foregoing experiments that the distribution in latex of the acids in the alcohol extract of dried films from

TABLE 4

ACIDIC COMPONENTS IN LATEX

| | Acids present (as mg. KOH) in | | | | |
|---|---|---|---|---|---|
| Particulars of acids | Ceylon parent latex (T.S. 41.2 per cent) | Ceylon centrifuged concentrate (T.S. 62.6 per cent) | Ceylon centrifuged skim (T.S. 26.0 per cent) | Malayan latex A (T.S. 42.6 per cent) | Malayan latex B (T.S. 42.6 per cent) |
| Ether-soluble fraction of alcohol extract | (per cent rubber) | (per cent rubber) | (per cent rubber) | (per cent rubber) | (per cent rubber) |
| (a) Free acids | 249 | 152 | 355 | 251 | 225 |
| (b) Combined acids (including water-soluble acids) | 181 | 187 | 222 | 194 | 204 |
| (c) Total acids | 430 | 339 | 577 | 455 | 429 |
| (d) Total ether-soluble acids | 289 | 237 | 435 | 259 | 295 |
| Water-soluble fraction of alcohol extract | (per cent water) | (per cent water) | (per cent water) | (per cent water) | (per cent water) |
| (a) Free acids | 258 | 251 | 265 | 230 | 242 |
| (b) Combined acids | 85 | 137 | 39 | 47 | 57 |
| (c) Total acids | 343 | 388 | 304 | 277 | 299 |
| Total water-soluble acids (including those in ether-soluble fraction) of extract | 407 | 545 | 346 | 418 | 390 |

ammonia-preserved latex is as follows. (1) The acids in the ether-soluble fraction of the extract are long-chain fat acids, of which about three-quarters are attached to the surface of the rubber particles at 20 per cent rubber content, and are the only acids in the alcohol extract so associated. Fat acids are present in ammoniated field latex to the extent of about 1 per cent of the total solids. (2) A smaller amount of mixed esters of water-soluble acids and fat acids, with the former greatly preponderating, is distributed throughout the mass of the rubber globules. Assuming a mean molecular weight of about 150, these combined acids are about 0.5 per cent of the latex total solids. (3) Over one-half the acids in the extract are water-soluble, present wholly in the water-phase of latex, presumably as ammonium salts. The serum also contains substances yielding acidic components on hydrolysis.

*Determination of acids in different latices.*—Examination of the alcohol extracts of dried latices for their content of free and combined acids and the separation of the former into ether-soluble and water-soluble fractions has so far been carried out on 25 experimental latices of known origin received from the Rubber Research Institute, Malaya, the Rubber Research Scheme, Ceylon, and through the courtesy of the Dunlop Rubber Co., Ltd. The results are set out in Tables 5 and 6, which deal with latices preserved with ammonia and sodium pentachlorophenate, respectively, and the sections are subdivided under the headings of unconcentrated latex, skim, centrifuged and creamed concentrates, respectively. The amount of each type of acid present is expressed in a manner which takes into account the conclusions reached regarding their situation in latex. Thus, esters and free fat acids are expressed on the total solids less the amount of extract, as a near estimate of the rubber phase, and free water-soluble acids are expressed on the water of the latex (*i.e.*, 100-T.S. per cent).

*Ammonia-preserved latices (Samples 1 to 18): confirmation of previous results.*—Considering for the moment only latices preserved with ammonia (1 to 18), it will be seen that there is little variation in the ester value (Table 5,

column 5) irrespective of particle size, confirming that these substances exist mainly in the rubber phase and not at the surface. The free fat acids, however, exist mainly at the surface of the globules, and it will be observed in confirmation of this statement that centrifuged concentrates (largest particles and least surface) contain less ether-soluble acids (column 6) than creamed concentrates (containing most of the particles), which in turn contain less than unconcentrated latices containing all the particles. The largest proportion of free ether-soluble acid is found in centrifuge skim which contains small particles and the largest surface per gram of rubber.

TABLE 5

ACIDS IN AMMONIA-LATICES

| Sample No. | Description | Total solids (per cent latex) | Total acids (per cent T.S.) | Ether-soluble (per cent rubber) | | Water-soluble acids (per cent water) |
|---|---|---|---|---|---|---|
| | | | | Combined acids | Free acids | |
| | (1) *Unconcentrated* | | | | | |
| 1 | Ceylon latex | 41.2 | 560 | 181 | 249 | 237 |
| | Ceylon latex, 7 months later | ... | 550 | 204 | 225 | 258 |
| 2 | Malaya latex heated 10 min. at 70° C | 42.6 | 538 | 194 | 251 | 230 |
| 3 | Control to 2 unheated | 42.6 | 532 | 204 | 225 | 242 |
| 4 | Malaya latex. Drum lined with titanium oxide latex film | 31.0 | 1029 | 174 | 237 | 360 |
| 5 | Same latex. Drum lined with zinc oxide-latex film | 30.9 | 1012 | 163 | 239 | 352 |
| 6 | Same latex. Drum lined with "quaker-wax" latex film | 30.8 | 1152 | 194 | 227 | 416 |
| 7 | Same latex, same lining. Drum completely filled | 30.8 | 1166 | 179 | 214 | 433 |
| 8 | Latex cleaned by light centrifuging | 44.0 | 869 | 178 | 222 | 522 |
| 9 | Malaya latex from fresh tapping cut | 55.9 | 360 | 168 | 223 | 194 |
| | (2) *Skim latex* | | | | | |
| 10 | Skim from centrifuging sample 1 | 26.0 | 1052 | 222 | 355 | 265 |
| | (3) *Centrifuged concentrates* | | | | | |
| 11 | From sample 1 | 62.6 | 295 | 187 | 152 | 251 |
| 12 | Dunlop latex of high Z.O.T. number | 60.5 | 460 | 172 | 188 | 567 |
| 13 | Ditto | 61.0 | 479 | 173 | 176 | 487 |
| 14 | Dunlop latex of low Z.O.T. number (doubly centrifuged) | 60.9 | 270 | 185 | 154 | 254 |
| 15 | Dunlop latex of low Z.O.T. number | 61.2 | 323 | 170 | 159 | 270 |
| 16 | R.R.I. latex; control to sample 23 | 62.2 | 309 | 198 | 179 | 235 |
| | (4) *Creamed concentrates* | | | | | |
| 17 | R.R.I. latex; control to sample 25 | 55.0 | 602 | 179 | 218 | 487 |
| 18 | From sample 1 creamed with sodium alginate | 57.7 | 486 | 180 | 206 | 398 |

TABLE 6

ACIDS IN SODIUM PENTACHLOROPHENATE LATICES

| Sample No. | Description | Total solids (per cent latex) | Total acids (per cent T.S.) | Ether-soluble (per cent rubber) | | Water-soluble acids (per cent water) |
|---|---|---|---|---|---|---|
| | | | | Combined acids | Free acids | |
| | (1) *Unconcentrated* | | | | | |
| 19 | 1 per cent preservative; heated 10 min. | 41.3 | 212 | 434 | 169 | 42 |
| 20 | Control to sample 19; no heating (partly coagulated) | 34.3 | 401 | 421 | 424 | 19 |
| 21 | 1.25 per cent preservative | 42.8 | 235 | 384 | 249 | 8 |
| 22 | 1.5 per cent preservative | 42.4 | 198 | 445 | 217 | 2 |
| | (2) *Centrifuged concentrates* | | | | | |
| 23 | 0.1 per cent NH$_3$; 0.3 per cent sodium pentachlorophenate | 61.4 | 306 | 152 | 237 | 129 |
| 24 | 0.1 per cent NH$_3$; 0.1 per cent sodium pentachlorophenate | 59.6 | 355 | 110 | 154 | 305 |
| | (3) *Creamed concentrates* | | | | | |
| 25 | 0.1 per cent NH$_3$; 0.3 per cent sodium pentachlorophenate creamed with tragon seed gum | 54.3 | 495 | 162 | 311 | 246 |

For a given type of ammoniated latex, there is little variation in free fat acids (column 6), suggesting that there is little variation in the average particle size of a given type of latex. In fact, it is possible to deduce the treatment which latex has received from the free ether-soluble acid value, and to calculate the relative average diameters resulting from different treatments.

*Variation in water-soluble acids.*—The outstanding feature of the results is the remarkable variation in the concentration of water-soluble acids in the latex serum, which are mainly responsible for the variation in the total acids (Table 5, column 4), some latices containing as much as three times the proportion of water-soluble acids dissolved in the serum as others. This variation will now be discussed in relation to the nature of the samples, and a few of the minor factors which influence it will be pointed out.

The changes occurring in sample 1 over a period of 7 months are small, and are probably not much beyond the limits of experimental error. Samples 2 and 3 were intended to show the influence of a short period of heating, designed to inhibit enzymatic activity, on the formation of acids during storage. Although differences were observable in the East shortly after preparation, these latices were very similar in properties on arrival in this country, in agreement with the results given in the table. Samples 4 to 7 were prepared to determine the effect of different drum linings on the properties of latex, and represent the same latex stored in drums lined, respectively, with a titanium oxide-latex film, zinc oxide-latex film and a chlorinated naphthalene wax; sample 7 was contained in a drum completely filled with latex, to determine the effect of reducing the amount of air in contact with the latex to a minimum. It will be seen that there were less water-soluble acids in samples 4 and 5, presumably due to the formation of zinc and titanium salts. It was found that the amount of zinc in solution was in reasonable agreement with this suggestion. Sample 9, latex from a freshly opened tapping cut, was of much

higher dry rubber content than normal field latex and, when dried, gave a distinctly yellow film.   The concentration of water-soluble acids was the lowest so far obtained for ammoniated latex, but the acids associated with the rubber were normal.   Samples 8 and 9 make an interesting contrast, since the former contained nearly three times the concentration of water-soluble acids in the serum.

The centrifuged concentrates 11 to 16 show the same range of variation in water-soluble acids and the same constancy in acids associated with the rubber as the unconcentrated latices.   The most interesting feature of the results in this section, however, is the correlation between the water-soluble acids and the Dunlop Z.O.T. number, which indicates that the variation in water-soluble acids is of practical importance in connection with the thickening of latex in the presence of zinc oxide.

The two creamed latices, 17 and 18, both have a high water-soluble acid concentration and, in the case of sample 18, belonging to the series of latices from the same parent latex, which has been discussed in detail in the previous section, a marked increase in water-soluble acids has occurred over the others in the series (samples 1, 10, 11).   It is possible that some decomposition of the creaming agent, sodium alginate, has occurred by the influence of ammonia, resulting in the formation of water-soluble acids.

*Sodium pentachlorophenate preserved latex*.—Samples 19 to 22 were Malayan latices preserved with from 1.0 to 1.5 per cent of sodium pentachlorophenate, which is a neutral substance readily soluble in water to give stable solutions, but because of the method of manufacture, the commercial product contains a little free alkali.   The latices were consequently slightly on the alkaline side of neutrality, with pH about 8.   The resistance of the latices to coagulation by friction varied with small differences in pH, both samples 19 and 20, containing 1 per cent preservative, being especially susceptible to coagulation of the froth produced on shaking the samples.   This tendency was greatly reduced in sample 21, and in sample 22 was scarcely noticeable.   Sample 20 had largely coagulated before it could be examined, so that the results obtained are probably representative of the smaller particles in the latex.

Latices preserved entirely with sodium pentachlorophenate are remarkable for their low content of water-soluble acids, the values for which range from 2 to 42, in striking contrast to those for ammoniated latices, which range from 194 to 567.   Water-soluble acids are consequently unlikely to be present in fresh latex, and are probably formed by decomposition of nonrubber substances under alkaline conditions.   It is thus evident that the great value of sodium pentachlorophenate as a preservative is that it is a substance practically neutral and, although it is desirable to have a little ammonia present in addition, to reduce viscosity and to render the latex less sensitive to coagulation by friction, the reduced alkalinity of the latex greatly restricts the decomposition of nonrubber substances to form water-soluble acids, which have been shown to promote the solution of zinc in compounded latex, giving rise to thickening[4].

Although esters associated with the rubber in latex preserved with sodium pentachlorophenate are relatively high, their decomposition can account only for a fraction of the largest amount of water-soluble acids in ammoniated latices, even though the esters are largely composed of water-soluble acids. Direct evidence that water-soluble acids are formed by hydrolysis of substances in the aqueous phase, as well as from esters in the rubber phase, is given by a comparison of the results for latices preserved with 0.1 per cent ammonia

and 0.3 per cent sodium pentachlorophenate (samples 23 and 25) with those for their respective controls (samples 16 and 17). The ester values are very similar for the four samples, but the amount of water-soluble acids present in the latices containing the mixed preservative is in each case about one-half that in the control ammoniated latices.

The most important conclusions to be drawn from the results obtained on the 25 latices examined are as follows.

(1) Water-soluble acids are almost absent in latex preserved with sodium pentachlorophenate alone, but vary considerably, and are the only variable components found in any particular type of ammoniated latex.

(2) Latices which thicken considerable in the presence of zinc oxide (high Z.O.T. number) have a high concentration of water-soluble acids, whereas those which do not thicken appreciably (low Z.O.T. number latices) have low concentrations of water-soluble acids.

(3) The formation of water-soluble acids is promoted by ammonia in proportion to the amount present, but not by sodium pentachlorophenate (neutral preservative), while a mixture of 0.1 per cent ammonia and 0.3 per cent sodium pentachlorophenate forms water-soluble acids in latex at about one-half the rate of ammonia alone (0.7 per cent).

(4) The decomposition of esters does not nearly account for all the water-soluble acids formed. The hydrolytic decomposition of proteins is likely to be an important factor.

(5) In latices containing at least 0.1 per cent ammonia, there is little variation in combined acids, irrespective of particle size, indicating that they exist mainly in the rubber phase and not at the surface, but their amount is less than half that in sodium pentachlorophenate latex, indicating that the compounds in which they are combined are hydrolyzed under alkaline conditions.

(6) The free fat acids exist mainly at the surface of the rubber globules in ammoniated latex, so centrifuged concentrates (containing the largest particles and least surface) contain less ether-soluble acids than creamed concentrates (containing most of the particles), which in turn contain less than unconcentrated latices containing all the particles.

(7) For a given type of latex, there is little variation in free ether-soluble acids, indicating that there is little variation in the average particle size of latices.

(8) Ammonia is an undesirable preservative insofar as it favors the decomposition of nonrubber substances to form salts of water-soluble acids, which promote the solution of zinc in compounded latex, and thus give rise to thickening. In the presence of a neutral preservative, such as sodium pentachlorophenate, these decompositions are greatly restricted.

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## APPENDIX A

### DETERMINATION OF ACIDS

Sufficient latex to give 30 grams of total solids is poured on to a level glass plate and dried at 30° C for about 40 hours, the air being kept moving at least

until the film is clear.    It is then removed and blended by passage through
cold rolls.    Portions weighing slightly in excess of 5 grams are sheeted thin
by passage through tightly closed rolls and finally are trimmed accurately to
within one or two milligrams of 5 grams.    The weighed samples are lightly
rolled in butter muslin, previously extracted with alcohol, placed in soxhlet
thimbles, and extracted for 20 hours in the dark with 50 cc. of rectified spirit
in a battery of six extractors of the type described in British Standard Specifi-
cation No. 902 for testing raw rubber.

Total acidity is determined by titration of the hot extract with $N$ alcoholic
potash in the presence of 5 drops of 1 per cent phenolphthalein solution, using
a 1 cc. burette capable of reading to 0.001 cc.    The temperature of titration
makes a considerable difference to the sensitivity of the end-point, which in
the cold is ill-defined in the presence of large amounts of water-soluble acids
forming salts insoluble in alcohol.    Total acidity is determined on three sam-
ples, from each of which the alcohol is removed by distillation, and the extracts
dried at 90° C for 2 hours.    The weight of extract is calculated after due
allowance has been made for added potash.

The alcohol is removed from the remaining three extracts without previous
titration, and the last traces are removed by rotating the flask in a nearly
horizontal position over a boiling water bath.    The extract is then sufficiently
dry to set solid on cooling, and to it is added 25 cc. of ether, the flask gently
shaken to swill the liquid round, and the ether solution decanted into a weighed
50 cc. or 100 cc. flask constructed of alkali-resistant glass, through a cotton-
wool plug placed in a funnel, and the process repeated with a further 10 cc. of
ether, which is added to the previous solution, and the plug squeezed free of
ether with a glass rod.    Ether is then distilled off, the flask is dried for 1 hour
at 90° C, and weighed to give the ether-soluble portion of the alcohol extract.

Acidity is determined, after the addition of 0.5 cc. of alcohol and warming
on the water bath to dissolve the extract, by titration as before with $N$ alco-
holic potash from a full 1 cc. of microburette.

After titration, the remainder of the 1 cc. of $N$ alcoholic potash is run in,
making the solution in the flask approximately 0.5 $N$, the flask and contents
are then heated under an air condenser 1 hour over a boiling water bath, and
the potash corresponding to combined acids is determined by back titration
with $N$ HCl from a 1 cc. burette fitted with a fine jet with waxed tip delivering
a drop of about 0.012 cc. volume.

If the method is used as a routine quality test for latex, the water-soluble
acids alone must be determined and, consequently, the determination of the
weight of the extract and that of the ether-soluble portion can be omitted, as
well as the estimation of combined acids.

## APPENDIX B

### DISTRIBUTION TECHNIQUE

Distribution data are obtained by the method described in the previous
paper (*loc. cit.*) at 20 per cent dry rubber content of the latex-sodium alginate
creaming mixture for 38 to 40 per cent field latex, and at about 29 to 30 per cent
dry rubber content for 58 to 60 per cent concentrated latices, *i.e.*, at corre-
sponding dilution of the serum.    It is not usually convenient to conduct
alcohol extractions on the underlayer, and distribution calculations of acids
are made from determinations on the dried whole latex and cream.    The deter-
minations necessary to calculate the distribution of acids between rubber and

water are the acid values of the whole latex and of cream, and the total solids of creaming mixture, cream and underlayer. The calculation will be illustrated by an actual example.

Acid value of whole latex (mg. KOH per 100 g. total solids of cream) 560
" " " cream " (mg. KOH per 100 g. total solids of cream) 252
Total solids (percentage of creaming mixture) 21.79
" " ( " " underlayer) 2.89
" " ( " " cream) 57.00

Let there be $x$.g. of cream from 100 g. of creaming mixture:
Then

$$\frac{57.00}{100}x + \frac{2.89}{100}(100 - x) = 21.79$$

Whence

$$x = \frac{18.90 \times 100}{54.11} = 34.93$$

Hence 100 g. of latex containing 21.79 g. of solids separated into 34.93 g. of cream containing

$$\frac{34.93 \times 57.00}{100} = 19.91 \text{ g.}$$

of solids and 63.07 g. of rubber-free underlayer containing 1.88 g. of solids.

The distribution of acids between rubber and water is now calculated as follows:

Total free acids in 100 g. of latex are equivalent to $560 \times .2179 = 122.1$ mg. KOH

Free acids in 34.93 g. cream are equivalent to $252 \times .1991 = 50.2$ mg. KOH

∴ Free acids in $(63.07 - 1.88) = 61.19$ g. water are $122.0 - 50.2 = 71.8$ mg. KOH

and

Free acids in $(100 - 21.79) = 78.21$ g. water are $71.8 \times \frac{78.29}{61.11} = 91.8$ mg. KOH

Now the rubber phase in 100 g. latex $= 21.79 - \left(\frac{78.21}{61.19} \times 1.88\right)$

$$= 21.79 - 2.40$$
$$= 19.39 \text{ g.}$$

∴ Free acids equivalent to $122.0 - 91.8 = 30.2$ mg. KOH are associated with 19.39 g. of rubber phase.

Whence the acid value associated with 100 g. of rubber phase

$$= \frac{30.2}{19.39} = 156$$

and the acid value of the alcohol-soluble substances in 100 g. of water

$$= 91.8 \times \frac{100}{78.21} = 117$$

Similar calculations apply to the determination of the other distributions, *i.e.*, the free and combined acids of the ether-soluble fraction of the alcohol extract, the alcohol extract itself and its ether-soluble fraction.

*Accuracy of the method.*—The method was developed by using a good quality 40 per cent latex, and the standard deviation of 12 determinations of total acid value averaging 560 was 8, and that of 14 determinations of the acid value of the ether-soluble fraction averaging 225 was 10. In the subsequent application of the method to 25 different latices of all types, the standard deviations of determinations in triplicate of acid values averaged for the 25 latices, 10 for an average value of 545 for the whole extract, 7 for an average of 206 for the ether-soluble portion, and 8.5 for an average value of 202 for the combined acids. These results show that the true result is unlikely to lie outside the mean ±4 per cent for total free acids; ±7 per cent for ether-soluble free acids, and ±9 per cent for combined acids.

As a consequence of variations of this order, the results of distribution experiments are probably accurate only to within a variation of about 20 per cent; and are of chief value in detecting large differences in the nonrubber distributions, such as occur, for instance, between latices preserved with ammonia and sodium pentachlorophenate, respectively. This point is illustrated by the results given in Table 7, where distributions are calculated in three

TABLE 7

| | Accuracy of distribution calculations | | | |
| --- | --- | --- | --- | --- |
| Method of calculation | Alcohol extract associated with rubber | Acid value associated with rubber | Alcohol extract associated with water | Acid value associated with water |
| | Per cent rubber | | Per cent water | |
| 1 | 2.54 | 165 | 1.92 | 114 |
| 2 | 2.28 | 161 | 2.10 | 117 |
| 3 | 2.74 | 195 | 1.85 | 106 |

ways: (1) taking the mean of about 12 determinations of each value; (2) taking the highest value for whole latex and the lowest value for the cream, and (3) *vice versa*.

## APPENDIX C

### CHEMICAL EXAMINATION OF THE ALCOHOL EXTRACT

The amount of material extracted from 38 to 40 per cent ammoniated-latex with alcohol by the technique described in Appendix A is usually between 8 and 10 per cent of the total solids, of which from 2 to 3 per cent is readily soluble in cold ethyl ether. To supplement the information already given in the text of the paper about the acids present, a brief chemical examination was made of the extract from a latex of good quality and from centrifuged skim from the same latex (samples 1 and 10, Table 5).

The alcohol extract of sample 1 was 8.4 per cent of the latex total solids, and was found to contain nitrogen and phosphorus, present in the fraction insoluble in ether, and amounting to about 2 and 3 per cent of the extract, respectively. The ether-soluble fraction amounted to 2.4 per cent of the latex total solids, and since it has been shown to contain all the substances associated with the rubber phase, would be expected to contain fat acids, sterols, lipin, and possibly other substances. The higher fat acids occurring in dry rubber have been shown by other workers to be linoleic, oleic, stearic and palmitic acids, and it is probable that the free acids in the ether-soluble fraction are also higher fat acids, since thorough washing with water of the ether solution failed to reduce its acidity. Thus, 97 per cent of the acidity of the ether solution remained under conditions where control experiments indicated

that ether retained 97 per cent of added oleic acid, 78 per cent of caproic acid (solubility in water 0.4 per cent) and 22 per cent of butyric acid (solubility in water 5.4 per cent).

It is probable that the phospholipin of latex is largely hydrolyzed in commercial ammoniated latex, since the ether-soluble fraction contained only a trace of phosphorus, and it has been shown that the amount of combined fat acids available for release by continued hydrolysis is small (Table 4).

The iodine value of the ether-soluble fraction was found to be 137.2 under conditions where the iodine values of oleic and linoleic acids were 89.9 and 181.2, respectively. This is much more than would be expected from the amount of unsaturated fat acids present, and indicates that either the fraction as a whole is highly unsaturated or reducing agents are present.

The residue insoluble in ether amounted to 6.0 per cent of the total solids, and contained the nitrogen and phosphorus of the alcohol extract, a part of which may have been organic phosphorus. Crystalline material, consisting of quebrachitol, nearly neutral denatured protein substances, and mineral substances amounted to 1.4 per cent, and the remaining 4.6 per cent was soluble in alcohol and water, in which it had a distinctly acid reaction (pH 4.5 in 1 per cent solution) and contained 2.9 per cent nitrogen, of which one-fifth was basic nitrogen, removable with dilute caustic soda, indicating the presence of protenic degradation products and possibly nitrogenous bases. A negative reaction with Nessler's reagent, however, indicated that ammonium salts were absent, and an increased titre obtained on addition of dilute formaldehyde to the aqueous solution suggested the presence of amino-acid groupings, which from the solubility of the material in alcohol are probably not present in the free state unless the presence of other substances greatly modifies the solubility. In this connection it may be noted that latex protein B of Bondy and Freundlich[5] is not precipitated by alcohol, and that phosphate ions exert a peptizing effect on protein solutions. The above general conclusions regarding the nature of the substances present in the ether-insoluble fraction were confirmed as a result of determination of nitrogen, color and precipitation tests for protein substances made on the corresponding fraction obtained from a sample of centrifuged skim (sample 10), and to confirm the chemical indications of the presence of amino-acid groupings occurring as degraded protein, a careful electrometric titration was carried out both in the presence and absence of formaldehyde. The ether-insoluble fraction of the extract from 10 grams total solids was dissolved in a weighed amount of molar potassium chloride, prepared from boiled distilled water to eliminate carbon dioxide, a known quantity of $N$ hydrochloric acid was added to reduce the pH to below 2, and the solution titrated with 0.5 $N$ caustic potash up to about pH 12, readings being taken at intervals of about 0.1 pH. The experiment was then repeated in the absence of extract, and in this way there was obtained an "extract" curve and a "blank" curve. The corrected curve for the extract was obtained by first ascertaining the "blank" titre at each pH reading on the "extract" curve, and subtracting it from the "extract" titre at this pH. The titrations were carried out in molar potassium chloride (*i.e.*, in excess) to offset changes in the ionic product of water, due to the formation of potassium chloride during titration[6]

Both experiments were then repeated in molar potassium chloride containing about 15 per cent formaldehyde, using the same quantity of acid to reduce the pH of the solution before titration with potash, and the corrected curve under these conditions was obtained in a similar manner.

The "blank" and "extract" curves in the absence of formaldehyde are given in Figure 1, and the two corrected curves for the extract in the absence (A) and in the presence (B) of formaldehyde are given in Figure 2.
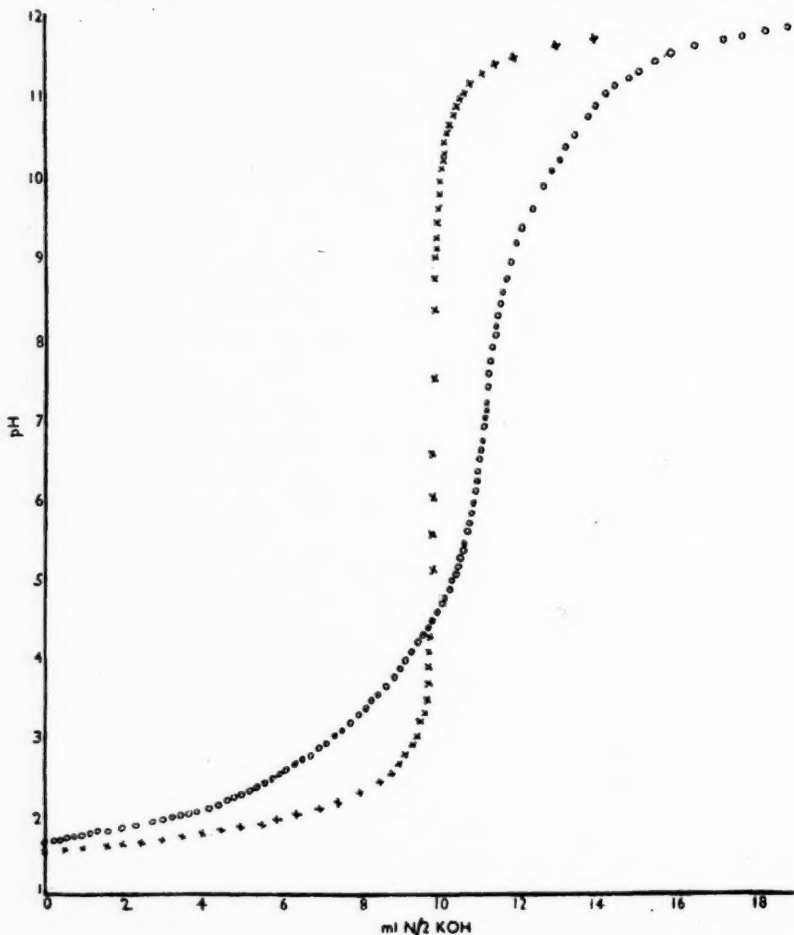


FIG. 1.—Titration in molar KCl of the water-soluble components in the alcohol extract of dried, centrifuged, skim latex (Sample 10, Table 5).
x x x   molar KCl alone.                    o o o   molar KCl plus extract.

The following comments are made on the results.

The natural pH of the solution was 4.36 in the absence, and 4.44 in the presence of formaldehyde, and the "blank" and "extract" curves in Figures 1 and 2 intersect at these respective pH values, indicating that there are more acidic than basic groups, and that the titrations are accurate.

In the absence of formaldehyde, a smooth curve was obtained (curve A, Figure 2) with three points of inflection, occurring approximately at pH values of 2.0, 7.5 and 11.6.    The curve shows a striking similarity in form to the titration curves for proteins, e.g., to that of gelatin[7], and is confirmation of the protein origin of the water-soluble acids.

The titre from pH 7.5 to 2.0 is 4.5 cc. of 0.5 $N$ HCl and from 7.5 to 11.6 is 2.6 cc. of 0.5 $N$ KOH.   The preponderating titre is, therefore, between pH 7.5 and 2.0, and since the natural pH of the solution is acid, this part of the curve represents approximately the titration of acidic groups, and that above pH 7.5 the titration of basic groups.   This is possible owing to the "zwitterion" nature
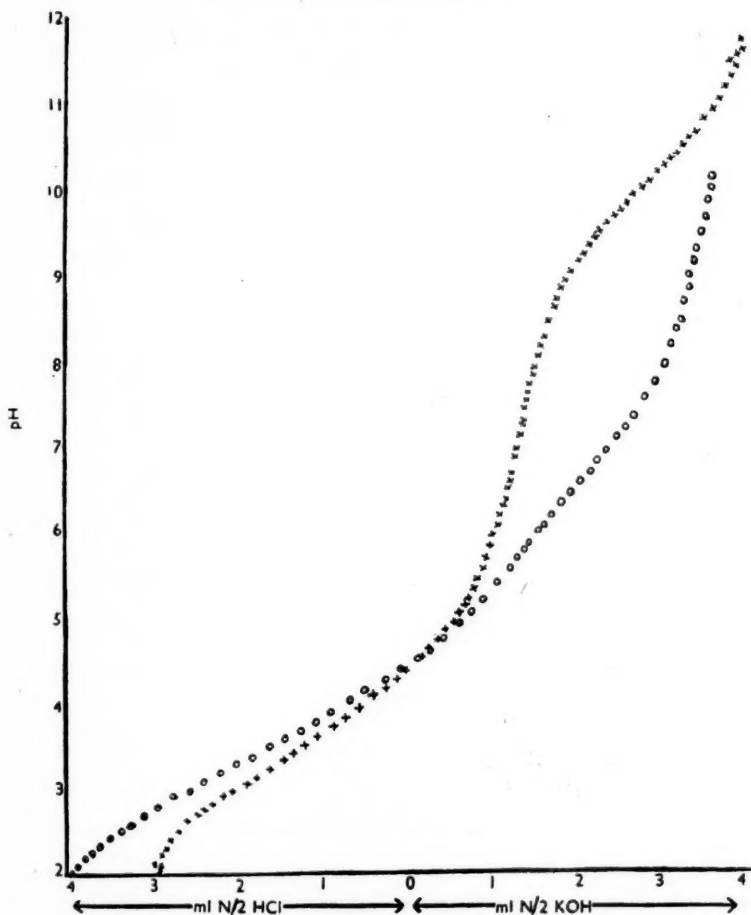


Fig. 2.—The effect of formaldehyde on the titration curve in molar KCl of the water-soluble constituents in the alcohol extract of dried centrifuged skim latex (Sample 10, Table 5).   Curve A is the resultant of the curves in figure 1, and curve B is obtained in a similar manner from curves not shown.
x x x   curve A (no formaldehyde).          o o o   curve B (15% formaldehyde).

of the amino-acid groupings in the protein molecules, each basic and acidic centre in the molecule being fully ionized[8].   In such cases the lower portion of the curve, therefore, represents the back titration of acidic (carboxyl) groups, and the upper portion the back titration of basic (amino or other) groups according to the scheme:

$$N^{+}H_3 \cdot R \cdot COOH \xleftarrow{\text{HCl}} N^{+}H_3 \cdot R \cdot CO\overline{O} \xrightarrow{\text{KOH}} NH_2 \cdot R \cdot CO\overline{O} + H_2O$$

The curve between pH 2 and 7.5 may also include the back-titration of salts of organic acids.

In the presence of formaldehyde, the titration curves, either direct or back, of bases are shifted towards lower pH values, but acidic curves are shifted either not at all or very slightly towards lower pH values[8]. Curve B shows that the right-hand side of curve A has been considerably shifted towards lower pH values, confirming that it represents the back-titration of basic groups and, in the absence of ammonium salts, is due to amino acids and possibly nitrogenous bases. The shift of the basic curve in the presence of formaldehyde is due to the formation of more weakly basic components of the type of methylene derivatives, and the extent of the shift depends on the relative excess of formaldehyde present. Figure 2 shows that in the presence of 15 per cent formaldehyde the shift was so extensive as almost to eliminate the middle point of inflection.

The slight discrepancies between the two curves are probably mostly due to the large and consequently variable amounts of materials extracted from the total solids of skim latex (3 determinations ranged from 15.8 per cent to 16.5 per cent).

The "acidity" of the water-soluble substances is at present estimated by taking the difference between the titres in alcohol to a phenolphthalein end-point of the whole extract and the ether-soluble fraction. On this basis the water-soluble material in the skim latex was given an "acid value" of 750, which corresponds to 3.25 cc. of the caustic potash used in the preceding experiments, per 10 grams of extract. It is known that titration in alcohol with potash neutralizes only part of the acidic and basic groups; in fact the 3.25 cc. of potash is less than one-half the total titre given by curves A or B.

Unfortunately, however, attempts to estimate the basic and acidic groups separately by means of indicator titration methods failed, owing to the difficulty of judging the acidic end-point and, for want of a better method, therefore, the use of the present technique for comparing the water-soluble acids in different latices was continued.

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# THE BACTERIAL OXIDATION OF RUBBER*

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In studying the biological oxygen demand of sea water[1], it has been observed that rubber stoppers increase the amount of oxygen consumed. In fact, the small amount of rubber gasket exposed to the water in citrate of magnesia bottles perceptibly increases the amount of oxygen consumed after 5 to 10 days' incubation. Heat-sterilized as well as formaldehyde-preserved controls proved that the increased oxygen consumption is attributable to biological activity.

One-gram samples of various kinds of rubber, cut in small pieces to give a surface area of approximately 10 sq. cm., were placed in 160-cc. glass-stoppered bottles. After sterilizing in an autoclave at 120° C for 20 minutes, the bottles were filled with sterile water saturated with oxygen. Half the bottles were inoculated; the others were left sterile. Duplicate bottles were analyzed for oxygen immediately by the Winkler technique, and the others were incubated in the water bath for one to five days at 22° C, after which the amount of oxygen consumed was determined. It was necessary to decant or siphon the water from the rubber before treating it with the Winkler reagents because free iodine reacts with rubber.

Using samples of rubber stoppers, rubber tubing, pure-gum rubber, and Neoprene, it was found that, whereas 0.53 to 0.88 mg. per l. of oxygen was consumed in the sterile controls after 5 days' incubation, 5.11 to 6.74 mg. per l. of oxygen was consumed in the inoculated water. Similar results were obtained when the controls were preserved with 1.0 per cent of formaldehyde. That the increased oxygen consumption is caused by microörganisms is indicated by the fact that the rate of oxygen consumption increases exponentially with time typical of a growth-curve and, more convincingly, by the multiplication of microörganisms.

Realizing that most of the aforementioned rubber products contain sulfur and other oxidizable components used as fillers or impurities, the experiments were repeated with several samples of highly purified (unvulcanized) caoutchouc or latex obtained from the Goodyear Tire and Rubber Company. Small quantities dissolved in C.P. benzene were distributed in bottles, which were manipulated to form a thin film of purified rubber on the inside of the bottles as the benzene evaporated. After driving off all the benzene, the bottles were filled with oxygenated water. Following the incubation of inoculated water, it was found that 2 to 2.5 mg. of oxygen was consumed in the presence of 1 mg. of purified rubber. This, together with the production of carbon dioxide, which was estimated manometrically, indicated that most of the rubber was oxidized. Considering rubber to be $(C_5H_8)_x$, it would require about 3.3 mg. of oxygen to completely oxidize 1 mg. of rubber. Part of the rubber was converted into bacterial protoplasm, as shown by the number of bacteria which appeared. The perforation of thin films of rubber on agar and on glass slides immersed in culture solutions gives further proof that rubber is utilized by microörganisms.

Confirming the observations of Söhngen and Fol[2] and of Spence and van Niel[3], most of the rubber-oxidizing microörganisms which have been observed belong to the genus *Actinomyces* or *Proactinomyces*. Many of the latter utilize complex hydrocarbons, according to Umbreit[4]. Rubber-oxidizing *Mycobacterium* and *Pseudomonas* also were isolated from our enrichment cultures. The aerial mycelium of an unidentified mould virtually enveloped the moist rubber on which it was growing, and its substrate mycelium seemed to penetrate the rubber.

Using oxygen consumption with adequate controls as a criterion of their presence, rubber-oxidizing bacteria have been found to be quite widely distributed in the sea and in garden soil. Neither in nature nor in the laboratory do rubber-oxidizing microörganisms appear to require rubber or related hydrocarbons for their multiplication, but old pieces of rubber hose and the cracks in tires found in moist places proved to be good sources of cultures.

Besides showing that neither synthetic nor pure *Hevea* rubber is biologically inert, and proving that rubber-oxidizing microörganisms occur fairly abundantly in nature, the observations suggest that such microörganisms may play an important role in the deterioration of rubber products. The life of rubber products which come in contact with moisture may be prolonged if ways can be found to retard or prevent the activity of rubber-oxidizing microörganisms.

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# METHYLETHYL KETONE EXTRACTION OF RUBBER *

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The extraction of rubber samples with acetone as an analytical procedure is a classical method; its origin is almost lost in antiquity, at least from the viewpoint of the rubber technologist. It is a valuable procedure, not only for practical evaluation of rubber samples, but from theoretical considerations as well. Acetone is commonly regarded as a polar "nonsolvent" for rubber, although some slight swelling action on rubber samples has been reported[1].

Various investigators have carried out the extraction under differing conditions[2], and the results have been shown to vary somewhat with the treatment of the sample[3]. The procedure as commonly employed today is well standardized[4], and great reliance is placed by rubber chemists on the analytical data obtained.

The standard procedure, however, suffers from one serious drawback—the length of time necessary to obtain the desired data. With a large number of samples this factor is enormously magnified. When applied to plant control determinations, the disadvantage is too readily apparent.

One possible method of reducing this difficulty would be the substitution for acetone of some other solvent, perhaps of higher boiling point, which at the temperature of extraction would have a greater solvent action on the nonrubber components. It should therefore accomplish the desired extraction in a shorter time.

A solvent which suggested itself for this purpose was the next member of the ketone series, methylethyl ketone. Its solvent action is, in general, similar to that of acetone, and its boiling point (79.6° C) is sufficiently low so that any undesirable thermal effects on the rubber sample should be minimized. At the same time, the boiling point of methylethyl ketone is enough higher than the boiling point of acetone that its solvent power at the temperature of reflux might be expected to be considerably greater.

Only limited data are available concerning the solvent action of methylethyl ketone on rubber. This is probably due to the fact that only recently has this solvent become obtainable in large commercial quantities. Whitby[5] mentions that methylethyl ketone exerts a little swelling action on raw rubber, more so than acetone, and that diethyl ketone is a solvent of rubber.

Bloomfield and Farmer[6] mention that dialkyl ketones possess some "interesting solvent properties" for rubber, but they likewise give no data and do not mention methylethyl ketone specifically.

## EXTRACTION PROCEDURE

Three types of samples were included in this study: (1) three samples of raw rubber—smoked sheet, pale crepe, and flat bark crepe; (2) three samples of vulcanized rubber, and (3) two samples of reclaimed rubber. These samples were sheeted and otherwise treated according to the A.S.T.M. standard

method[4]. The methylethyl ketone was distilled over anhydrous potassium carbonate before use.

The acetone extractions were carried out under the conditions specified in the standard procedure, except as otherwise noted. The methylethyl ketone extractions were adjusted to the same rate of reflux and, except for the variations noted, were otherwise treated exactly the same as the acetone extractions. To eliminate the effects of other variables, all the extractions carried out under a given set of conditions were run side by side at the same time.

Two types of extraction were employed with methylethyl ketone—continuous and discontinuous. It has been previously shown that discontinuous extraction with acetone gives higher results than continuous extraction, presumably because of oxidation caused by the removal of the natural antioxidant by the acetone[7]. The samples were completely enclosed in filter paper and were, therefore, not directly exposed to light. No difficulty was experienced in obtaining a constant value for the acetone extract, which served as a control for the results with methylethyl ketone.

The experimental results are summarized in Table I, and are plotted in Figures 1 and 2. An experimental result given as Sw. indicates that the sample

TABLE I

ACETONE AND METHYLETHYL KETONE EXTRACTIONS

| | Acetone extraction (percentage) | | | | Methylethyl ketone extraction (percentage) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 2 hrs. | 2+2 hrs. | 2+2 +2 hrs. | 8 hrs. continuous | 2 hrs. | 2+2 hrs. | 2+2 +2 hrs. | 16 hrs. continuous | 24 hrs. continuous |
| Pale crepe | ... | 2.77 | 3.37 | 3.40 | 1.84 | 2.71 | 6.16 | 3.72 | 4.77 |
| Smoked sheet | ... | 2.70 | 2.73 | 2.76 | 1.86 | 2.50 | 3.09 | 4.93 | 8.62 |
| Flat bark crepe | 0.63 | 0.98 | 1.20 | 1.20 | 1.73 | 3.10 | 4.68 | Sw. | Sw. |
| Tread | 5.12 | 5.72 | 6.10 | 6.22 | 5.96 | 6.50 | 6.93 | 7.31 | 7.40 |
| Tube A | 4.77 | 5.02 | 5.32 | 5.45 | 6.18 | 6.50 | 7.03 | 7.29 | 8.44 |
| Tube B | 5.84 | 6.02 | 6.22 | 6.30 | 7.62 | 8.02 | 8.28 | 7.59 | 7.94 |
| Tire reclaim | 7.72 | 7.78 | 8.11 | 8.20 | 12.42 | 18.67 | 23.30 | 20.94 | 25.75 |
| Air-bag reclaim | 9.45 | 16.71 | 17.22 | 17.54 | 23.52 | 27.18 | 30.10 | 26.58 | 28.51 |
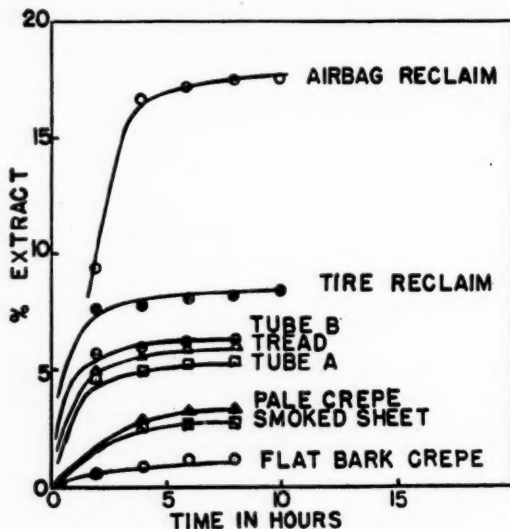


FIG. 1.—Acetone extracts of samples studied.
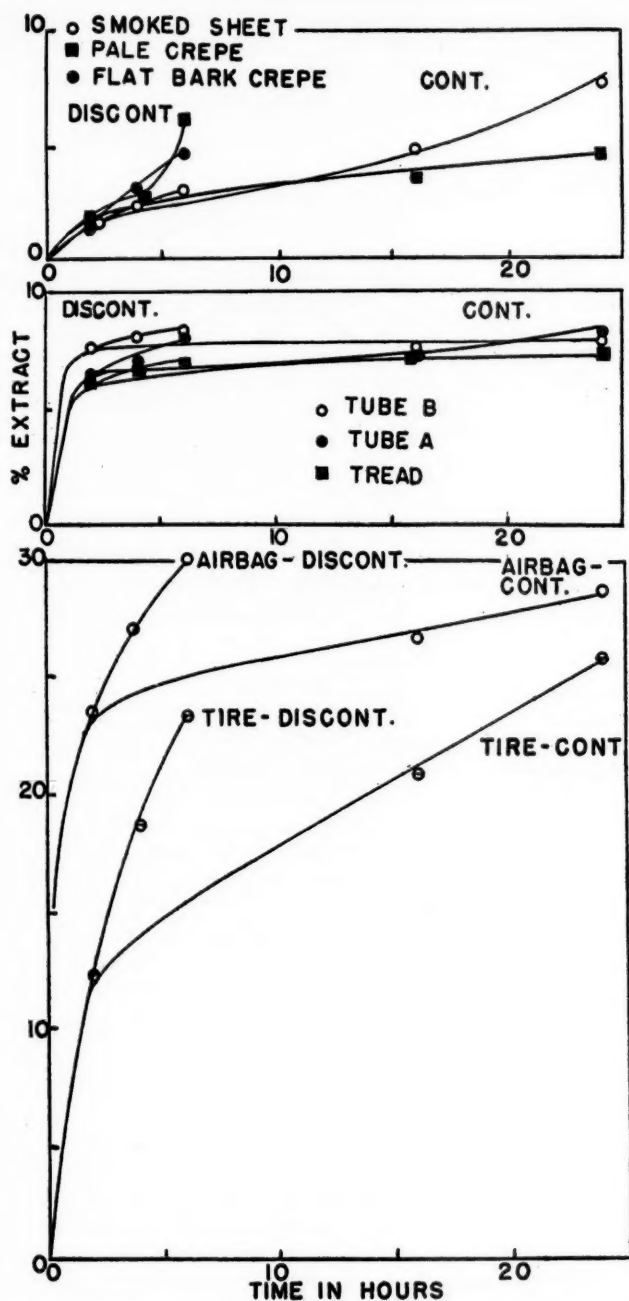
FIG. 2.—Methylethyl ketone extracts of raw rubber samples, vulcanized samples, and reclaim samples.

had been swollen enough by the liquid to render the extract figures valueless. In most cases the sample swelled to the point where it burst the filter paper thimble and then clogged shut the siphon tube in the extraction cup. When this point was reached, the determination was abandoned.

## SWELLING EFFECTS

The most outstanding result for crude rubber is the marked difference in rate of extraction of the flat bark crepe sample, which has the lowest extract with acetone but is swollen fairly rapidly by methylethyl ketone. The 4-hour methylethyl ketone extracts of the pale crepe and smoked sheet samples are only slightly greater than the corresponding acetone extracts. With longer extraction, however, the samples swell; the pale crepe swells more rapidly with discontinuous extraction, and the smoked sheet more rapidly with continuous extraction.

This swelling characteristic, which agrees with the observations of Whitby, is evidently concerned with the sol-gel equilibrium[8]. The first action of the methylethyl ketone is probably to remove the same nonrubber components as the acetone, after which it starts to swell the sol fraction of the rubber. Because of its polar character, it might be expected to exert a depolymerizing effect on the rubber molecule. It probably also removes the natural antioxidant and thus tends to shift the equilibrium toward the sol phase, as it has been clearly demonstrated that oxygen plays a major role in promoting this shift[9]. In this light, flat bark crepe, because of its variable history, might be expected to give higher extract values, since it would undoubtedly be subjected to more oxidation and depolymerization during its previous treatment.

The vulcanized samples show the same general trend, although the swelling tendency is repressed, as would be expected. The differences between continuous and discontinuous extraction are less pronounced. The tread stock is the only one of the three which seems to approach a value which is fairly constant for both continuous and discontinuous extraction.

The experimental results for the reclaim samples are even more interesting. Both samples show large extract values, which increase even more rapidly with discontinuous extraction than do any of the samples previously noted. The methylethyl ketone extract at the end of 2 hours is larger for either sample than the acetone extract after repeated extraction.

These unusually high values recall the behavior of reclaim with chloroform, as noted by Stafford[10] and studied in more detail by Weber, Winkleman, and others[11]. These investigators have well established the postulate that the chloroform extract consists chiefly of depolymerized rubber. It was further shown that there is a definite distribution of the combined sulfur, most of it remaining in the chloroform-insoluble portion. As shown by the work of Hauser and his coworkers[12], vulcanization to optimum cure apparently takes place with minimum loss of unsaturation. The portion of the molecule which has combined with sulfur is then insoluble in chloroform, either because of this combination or simply because the sulfur linkage provides it with a higher molecular weight. The uncombined portion is still unsaturated, and hence susceptible of oxidation. The action of oxygen would depolymerize it and increase the solubility.

As indicated by these results, especially when the entire set of data is considered together, it appears that the general solvent action of methylethyl ketone is somewhat similar to that of chloroform. It apparently acts as a

solvent for some of the lower molecular weight fractions. It also seems to act as a solvent for the antioxidants, both natural and added, so that discontinuous extraction results in a much greater oxidative depolymerization of the rubber and a shift toward the sol phase.

This general selective solvent character of the methylethyl ketone for rubber fractions of certain molecular weight is in agreement with observed results with other high polymers. Vinyl chloride polymers of certain molecular weight ranges, for instance, are dissolved by methylethyl ketone, whereas the same fractions are insoluble in acetone.

A study of these data in terms of the original problem indicates that methylethyl ketone could not be satisfactorily substituted for acetone in the classical extraction procedure, even if under certain conditions with a given sample the same values might be obtained. The results across a series of samples show too much variation.

The data submitted in this report, however, indicate that methylethyl ketone may prove to be a useful research tool in studying the fractionation of rubber and similar problems.

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# THE PERMEABILITY OF RUBBER TO WATER VAPOR *

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## INTRODUCTION

In connection with a study of various kinds of vulcanized rubber, including rubber films from vulcanized latex and latex films vulcanized in the dry state, it seemed desirable to investigate the packing of the latex particles. To what extent, for example, are these still present or are they coalesced?

It is known that the diffusion of water vapor through solid substances may give an indication of the internal structure of matter[1]. With this in mind, a search was made for a simple method to determine the diffusion of water vapor through rubber; high accuracy was not required so much as were simplicity and adaptability to a long series of experiments.

Such a procedure was found in the method described by Hoekstra[2] for determining the permeability of varnish films to water vapor. A detailed description of the method is given later in this paper. More accurate methods of determination, applied to rubber, have previously been described by others[3], but these procedures are less suitable for systematic tests.

The diffusion of gases and vapors through a nonabsorbing substance is governed by Fick's law: $N = \dfrac{D\ A\ T}{x}\ (p_1 - p_2)$, where $N$ is the quantity of vapor or gas passing through; $A$ the area of the surface tested; $T$ the time during which the measured quantity of gas passes through; $x$ the thickness of the permeable layer; $p_1 - p_2$ the difference in vapor pressure on opposite sides of the permeable layer, and $D$ the diffusion constant.

The permeability of a substance to a gas is thus completely defined by $D$, irrespective of the conditions under which the measurements are made. The permeability increases with $D$, and *vice versa*.

If the sample, besides allowing gas to pass through, also absorbs some of it, Fick's law is no longer valid. In such a case the relations are so complicated that they cannot be expressed by a simple formula. It is already known from previous investigations[4] that, since rubber absorbs water vapor in noticeable quantities, the law of Fick cannot, strictly speaking, be applied. This means that when the permeability is determined under different conditions as regards the thickness of the test-specimen and(or) the vapor pressure differential, the diffusion constant calculated from the results varies. However, this difficulty can be largely overcome by always carrying out the determinations in approximately the same manner; the factor calculated from the results depends on the experimental conditions and can, therefore, not be called a diffusion constant. In the discussion which follows, this factor is termed the "permeability constant", and is designated by $P$. The permeability of different rubbers can then be compared by always calculating $P$ by means of Fick's law from the measurements. Since the absorption phenomena which cause the devia-

tion from Fick's law are independent of the time factor $T$ and the surface area $A$, $P$ to be calculated is characterized sufficiently by the applied pressure differential and the thickness of the sample. In addition, the temperature must, of course, be known.

## METHOD OF DETERMINATION

Special care is taken in the preparation of the rubber to be studied, which should be in the form of films between 0.4 and 0.6 mm., preferably 0.5 mm. thick. A disk having a diameter about 0.5 cm. larger than the cylindrical glass weighing dishes employed is cut out of the film with a Schopper punch. Water is run into the dish, the rubber film is fastened to it, and the measurements are made by determining the loss in weight of the dish when placed in a dry atmosphere. The rubber is fastened on the dish in the following manner (see also Figures 1 and 2). A small glass cup, into which about 1 cc. of water has been pipetted, is placed on the rubber disk. If water alone is employed, it is possible to use cups of aluminum foil, which can be prepared by fashioning the foil around the bottom of a test-tube. Then the upper rim of the weighing dish is dipped into melted asphalt. While the asphalt is still warm, the weighing dish is placed upside down on the rubber disk and firmly pressed on it. Then the dish is rapidly turned up, care being taken that none of the water comes in contact with the rubber.

The dishes thus sealed with rubber are placed in a desiccator containing silica gel. To be sure that the water vapor which escapes through the rubber into the desiccator is rapidly absorbed by the silica gel, the air in the desiccator is kept in motion by means of a fan driven by a small motor; the fan axle passes through the desiccator cover, and is made air-tight by means of a mercury seal (see Figure 2). The initial experiments showed plainly that it is desirable to keep the air in the desiccator in motion, for otherwise the results obtained are too low[5]. It may be advisable to place the desiccator in a thermostat, but this was not done in the present work because the limit of accuracy was considered sufficient for our purpose.

No measurements need be made during the first 24 hours, because at the start of the experiment, an equilibrium must be established between absorption by, and diffusion into, the rubber. The first weighing is therefore made after 24 hours; from then on the loss in weight is determined daily until an approximately constant loss per unit of time is observed. As a rule, weighings on 4 days are sufficient.

## ACCURACY

When measurements are made on the same days in the same series of tests, the accuracy is affected by errors in measuring the thickness, surface, weight, and time. The errors in all these measurements are quite small, even those in the weighings, since, even with the best rubber sample examined, it was found that there was always a loss in weight of about 5 mg. per 24 hours. The mean error of a single observation, for all of these measurements combined, is in the neighborhood of 2 per cent. When several series of measurements were made on the same sample, varying deviations, greater than the mean error just mentioned, were observed with different rubbers. This is not surprising, since the homogeneity of a rubber prepared from plasticized rubber by vulcanization in a mould in an autoclave may be expected to be quite different from that of a film of rubber obtained by drying latex. With latex
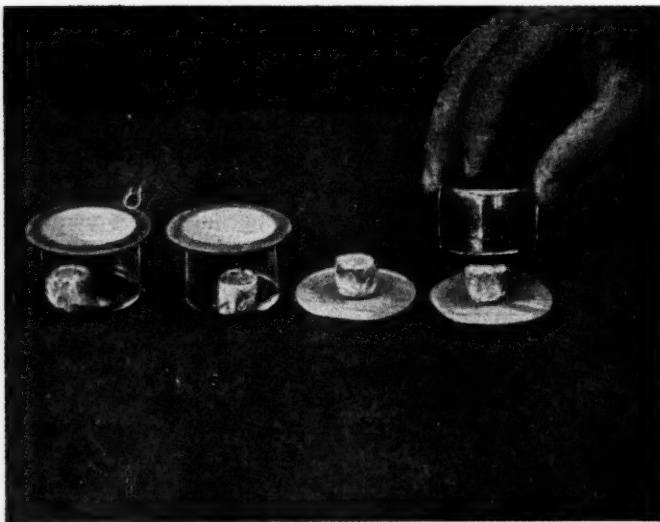
Fig. 1.—Right: the glass weighing dish, the upper edge of which has been dipped in asphalt, is placed on the rubber film upon which stands a small aluminum cup containing water. Left: the weighing dish has been turned up, and the water has run out of the cup.
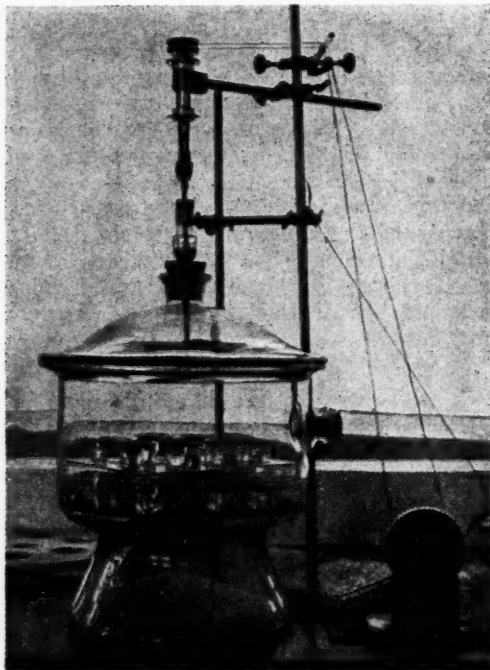


Fig. 2.—A set of permeability tests in the desiccator, with silica gel in the bottom; fan at top.

films, in duplicate series of tests with two different rubbers, each series consisting of twenty determinations, the mean error of a single observation was calculated to be from 9.2 to 7.3 per cent.   More favorable results, with a mean error of about 5 per cent, were obtained with samples prepared from mixtures which had been blended on a roll mill and vulcanized under pressure.

When measurements made on different days were compared, the results were further affected by the absence of a thermostat and the assumption that the average temperature was always 28° C.   The mean error due to this assumption was of about the same order of magnitude as that made in measurements in one series on the same day, caused by variations in the rubber (about 10 per cent).   Summarizing, the mean error of a single observation, under unfavorable conditions of measurement, was in the neighborhood of $\sqrt{10^2 + 10^2} \approx 14$ per cent.   Because of this low accuracy of a single observation, all determinations were made in triplicate, which increased the accuracy of the values to $14/\sqrt{3}$, i.e., about 8.5 per cent.

## APPLICABILITY OF FICK'S LAW

There is no doubt that the diffusion of water vapor is directly proportional to the surface area, and this point needs no further examination.   Proportionality with time was observed after one to three days.   The question still remained whether, and to what extent, there was direct proportionality with the vapor pressure and what was the effect of the thickness of the rubber.

### EFFECT OF THICKNESS

Taylor, Hermann and Kemp[4] have shown that the permeability constant increases with the thickness of the rubber.   For a certain soft rubber they found a fairly regular increase from 7.7 to 8.5 with increase in thickness from 0.04 cm. to 0.24 cm.   With a range in thickness from 0.4 to 0.6 mm., as was the case in our determinations, the constant should, under the same conditions, increase from 7.7 to 7.9.   This increase is within the limit of error of our measurements, so it cannot be accurately determined.

This agrees with the observations summarized in Table 1, which refer to

### TABLE 1

#### EFFECT OF THICKNESS ON THE PERMEABILITY CONSTANT

*Crepe rubber, prepared from*
  I. Field latex, one month old.
  II. Centrifuge cream, one week old.
  III. Fresh field-latex, ammoniated.
  IV. Latex, creamed four times, 2½ years old.
  V. Latex, purified according to Netherlands Patent Application No. 92,872.
Mixture: rubber 100, zinc oxide 6, sulfur 3.5, mercaptobenzothiazole 0.5, stearic acid 0.5; vulcanized 60 minutes at 127° C.

| Mixture from crepe No. | Thickness (mm.) | P | Thickness (mm.) | P | Thickness (mm.) | P |
|---|---|---|---|---|---|---|
| I | 0.37 | 6.4 | 0.38 | 6.6 | 0.87 | 7.3 |
| II | 0.39 | 6.1 | 0.49 | 6.2 | 0.64 | 6.1 |
| III | 0.40 | 6.8 | 0.52 | 7.1 | . . . | . . |
| IV | 0.41 | 5.4 | 0.67 | 5.2 | 0.93 | 5.3 |
| V | 0.44 | 5.5 | 0.55 | 6.0 | . . . | . . |

$P$ expressed in g. per cm. per hr. per mm. Hg $\times 10^{-8}$.
$p_1 - p_2 = 28.3$ mm. Hg.

vulcanized rubber prepared from crepe rubber from latices of very different properties. Three vulcanized films of increasing thickness were prepared from each kind of rubber, and three permeability determinations were carried out for each thickness. The average results of these are given in the table. In spite of considerable differences (nitrogen and ash content) in the purity of the rubbers, the differences in the permeability constants are very small, and no significant effect of the thickness of the samples is evident, although the differences in thickness are greater than would normally be the case. Still there is an evident tendency of $P$ to increase with thickness.

An analogous experiment was carried out by preparing mixtures in the latex state, drying them, and vulcanizing them in air. In this case the differences in thickness seem to have a greater effect and, at the same time, the important influence of the previous history and purification of the latex is evident (see Table 2).

### TABLE 2

#### EFFECT OF THICKNESS ON THE PERMEABILITY CONSTANT

*Latex films from the same latices as listed in Table 1*

Mixture: rubber 100, zinc oxide 2, sulfur 2, Vulcafor-SDC 0.8; mixture prepared in the latex state. Vulcanized 10 minutes at 120° C in air.

| Mixture from latex No. | Thickness (mm.) | $P$ | Thickness (mm.) | $P$ | Thickness (mm.) | $P$ |
|---|---|---|---|---|---|---|
| I | 0.37 | 42 | 0.68 | 63 | 0.90 | 60 |
| II | 0.46 | 27 | 0.64 | 32 | 0.81 | 26 |
| III | 0.35 | 14.0 | 0.58 | 15.8 | 0.77 | 16.4 |
| IV | 0.47 | 9.9 | 0.62 | 9.9 | 0.79 | 10.3 |
| V | 0.40 | 6.8 | 0.78 | 6.9 | 1.01 | 7.3 |

$P$ and $p_1 - p_2$ expressed as in Table 1.

Here too it is impossible to say to what extent the effect of thickness must be ascribed to absorption phenomena. There is no assurance whatever that a film obtained by drying 20 cc. of latex has the same structure as one of the same surface size, but obtained by drying 40 cc. of latex. In the latter case, drying requires a much longer time, and the ammonia will have evaporated while the water content of the membrane is still much higher than in the first case. The conditions with respect to the eletcrical charges on the latex particles are probably quite different during coagulation and, as a consequence, differences in the degree of packing, in other words in the structure, are by no means impossible. The extent to which reactions due to bacteria take place during drying also may play a part; hence the age of the latex may be of importance. In view of this, it is not surprising that the results in Table 2 show irregularities in the effect of the thickness.

Summarizing, the results of the two series of experiments show that, with variation in thickness between 0.4 and 0.6 mm., the effect of thickness on the diffusion of water vapor through a film prepared from plasticized mixtures may be neglected, because of the limited accuracy of the determination. In the case of latex films, the same variation in thickness may give rise to variations in the diffusion of water vapor, which are greater than the errors of observation, but it is still possible that these are due to actual differences in structure. In either case, diffusion of water vapor tends to increase with increase in thickness, in agreement with the observations of Taylor, Hermann and Kemp[4].

## EFFECT OF VAPOR PRESSURE

As stated in the introduction, experiments on this question may be carried out by creating different vapor pressures in the dishes, for example, by means of saturated salt solutions. Taylor, Hermann and Kemp[4] found with a certain rubber that a change in vapor pressure produces a change in the diffusion of water vapor in accordance with Fick's law as long as the vapor pressure is lower than around 20 mm. Hg. With higher vapor pressures, the calculated permeability constant increases.

Because of this observation, we endeavored to make all measurements below this critical vapor pressure so as to be able to determine the true diffusion constant. Several experiments proved, however (see Table 3), that as a

### TABLE 3

EFFECT OF THE DIFFERENCE IN VAPOR PRESSURE ON THE PERMEABILITY CONSTANT

*Rubber:*
I. Unvulcanized films from fresh centrifuge cream, prepared from field latex five months old.
II. Unvulcanized films from field latex one month old.
III. Vulcanized latex films, from centrifuge cream*.
IV. Vulcanized whole latex rubber (centrifuge cream), mixed on a mill*.

| $p_1$ (mm. Hg) $p_2 = 0.0$ mm. | Permeability constant | | | |
|---|---|---|---|---|
| | Rubber I | Rubber II | Rubber III | Rubber IV |
| 7.7 | 4.8 | ... | 4.1 | 3.9 |
| 13.0 | 5.2 | 4.7 | 4.5 | 4.8 |
| 13.3 | 5.3 | 5.0 | 5.0 | 5.0 |
| 16.3 | 7.3 | 7.4 | 5.6 | 5.7 |
| 21.1 | 8.6 | 14.3 | 5.7 | 5.7 |
| 22.2 | 8.2 (?) | 20.1 | 5.6 | 6.1 |
| 23.9 | 9.5 | 26.7 | 6.2 | 6.4 |
| 26.3 | 9.7 | 41.3 | 6.7 | 6.4 |
| 28.3 | 11.0 | 76 | 8.2 | 6.7 |

* Mixture: rubber 100, zinc oxide 6, sulfur 3.5, stearic acid 0.5, mercaptobenzothiazole 0.5; vulcanized 60 minutes at 127° C.

rule the diffusion constant does not attain a definite value. This must be due to the fact that the value calculated from the measurements depends on the method of determination. The deviation from Fick's law for latex films is considerable, especially in the unvulcanized state, and it increases with the impurities remaining in the latex. Latex films vulcanized in the dry state show only slight deviations, but rubber plasticized on a roll mill behaves very much like that reported by Taylor, Hermann and Kemp[4]. The disturbing fact is that the greatest relative differences between rubbers were found to be when the measurements were made in saturated water vapor. Determinations made under these conditions are apt to lead to unreliable results if water vapor condenses on the rubber. In that case the diffusion of water, not of water *vapor*, is measured. For this reason we placed a saturated solution of potassium sulfate in the dishes in most of our experiments; this means that, at 28° C, the measurements were made at a vapor pressure of 26.3 mm. of mercury. The objection might be raised against this procedure that it is generally preferable to use a lower relative humidity[5] in the testing of materials, and also in determinations of the diffusion of water vapor. But we decided not to do this because, at a lower vapor-pressure differential, the differences in the permeabilities of various rubbers are less pronounced.

## EXAMPLES OF APPLICATIONS

### (a) Addition of Substances to the Latex

Since various substances must be added in the preparation of vulcanized latex films, their effect on the diffusion of water vapor was investigated.

The addition of salts, such as sodium chloride, sodium pentachlorophenol or Vulcafor-SDC to latex brought about practically no change in the diffusion of water vapor through rubber films prepared with them. These tests were made with pressure differentials from 7.7 to 28.3 mm. of mercury. The addition of zinc oxide and sulfur as vulcanizing agents caused no change in the permeability constants.

On the contrary, a change was observed when certain compounds which alter the composition and properties of the adsorption film on the latex particles were added to latex. Thus, the addition of potassium hydroxide or other alkali caused an increase in the permeability constant, which must be ascribed to hydrolysis of the protein (cf. the effect of hydrolysis when latex is stored; see under c of this section). The permeability constant of a film from purified latex also increased greatly when, for example, casein was added to the latex. The addition of saponin likewise increased the permeability constants (see Table 4). The less the latex had been purified, the greater was the effect of this substance. However, the addition of soap in most cases had little or no effect.

### (b) Pretreatment of Films

The effect of the previous history of films on the water vapor diffusion constant was studied with unvulcanized and with vulcanized films prepared from various kinds of latex. Three pretreatments were investigated: (1) storing one week in air; (2) drying one week over silica gel; (3) storing one week above water.

The diffusion of water vapor was not affected by these treatments, as far as could be ascertained by the method of measurement employed. However, the period within which the loss in weight became constant was in some cases longer than normal.

Stretching or heating of unvulcanized rubber films, however, resulted in a considerable decrease in the diffusion of water vapor. This may be seen from the observations recorded in Table 4. Although stretching an unvulcanized film prepared from purified latex caused little change, the same treatment applied to a film obtained from normal centrifuge cream reduced the permeability to water vapor as much as one-half. It may be concluded from this that the channels along which water vapor diffuses are largely destroyed by stretching, due to coalescence of the latex particles during stretching. The film prepared from purified latex contains in the unstretched condition so few of these channels—it should perhaps be said the channels are already so narrow—that stretching has little effect. Films containing saponin show this same phenomenon particularly well. The conclusion that the continuity of structure of the adsorption films on the latex particles in the latex film is broken by stretching and that, at the same time, the latex particles in the rubber coalesce, is in agreement with the fact that a latex film containing saponin can be redispersed in water, but that this property is lost on stretching the film[6]. The effect of heating unvulcanized films in the absence of vulcanizing agents is similar to that of stretching, and depends markedly on the temperature to which they are heated. The observations show that at 110° C

latex particles coalesce to a greater extent than at 90° C. This behavior must be kept in mind when, in a later section, the permeability of vulcanized latex films is compared with that of unvulcanized films. If vulcanization is carried out at a higher temperature, this fact alone usually accounts for a lower permeability to water vapor. Under this condition, stretching and further heating of the vulcanized film has little or no effect. With films that have been vulcanized at room temperature or, in general, under conditions of vulcanization such that the latex particles can coalesce little or not at all, heating has a pronounced effect. This applies also to rubber prepared from vulcanized latex. These phenomena have not yet been fully investigated, however.

TABLE 4

EFFECT OF STRETCHING AND OF HEATING ON THE PERMEABILITY CONSTANT OF
UNVULCANIZED LATEX FILMS

| | Permeability constant (g. per cm. per hr. per mm. Hg × 10⁻⁸) | | | |
| | Purified latex | | Centrifuge cream | |
| Pretreatment of the latex films | Without addition | Plus saponin | Without addition | Plus saponin |
|---|---|---|---|---|
| No pretreatment | 9.0 | 15.9 | 21.2 | 147.0 |
| After stretching at 200% for 1 minute | 7.8 | 9.3 | 9.9 | 45.5 |
| After heating at 90° C for 30 minutes | 8.2 | 8.6 | 12.7 | 25.8 |
| After heating at 110° C for 30 minutes | 8.4 | 9.9 | 9.4 | 11.6 |

Purified latex: prepared according to Netherlands Patent Application No. 92,872; three months old.
Centrifuge cream: five months old.
Saponin added: two per cent on dry rubber.
$p_1 - p_2$: 26.3 mm. Hg.
Thickness of rubber film: 0.5 mm.

### (c) CHANGES IN LATEX DURING STORAGE; EFFECT OF PURIFICATION

When ammoniated field-latex is stored for increasing lengths of time and films are prepared from it by drying, the diffusion of water vapor through the vulcanized or unvulcanized films increases with the time of storage. The effect is greater in the case of unvulcanized films. Table 5 shows some results illustrating this point.

TABLE 5

EFFECT OF STORING AND OF PURIFYING LATEX ON THE PERMEABILITY OF
CRUDE AND VULCANIZED LATEX FILMS

| | Permeability constant[a] | | |
| | Unvulcanized | Vulcanized[b] | |
| Treatment of the latex | | as film | as latex |
|---|---|---|---|
| Ammoniated field-latex, one day old | 26 | 25 | 155 |
| Latex, centrifuged after nine days; cream stored for three weeks | 44 | 29 | 117 |
| Ammoniated field-latex, three months old | 101 | 40 | 143 |
| Ammoniated field-latex, centrifuged after three months; cream stored for three weeks | 19.1 | 18.0 | 48 |

[a] In g. per cm. per hr. per mm. Hg × 10⁻⁸.
$p_1 - p_2 = 26.3$ mm. Hg; $p_2 = 0.0$ mm. Hg.
[b] Mixture: rubber 100, zinc oxide 1.2, sulfur 1.6, Vulcafor-SDC 0.64.
Vulcanization: in form of film, 10 minutes at 120° C; in form of latex, 10 minutes at 80° C.

It follows from this that hydrolyzed protein components increase greatly the diffusion of water vapor. If it is intended to prepare a latex adapted to the manufacture of articles with low permeability to water vapor, it is advisable always to use purified latex (cream latex or centrifuge cream), and to delay the purification as long as possible so as to remove the largest possible quantity of protein and decomposition products.

### (d) Vulcanization

Table 5 shows also the effect of vulcanization of latex rubber. It is obvious that, for the samples listed, vulcanization in the latex state leads to very high permeability, which compares unfavorably with that obtained by vulcanization of dried latex mixtures in air. The difference is particularly noticeable with fresh latex. As has already been pointed out in part a of this section, vulcanizing agents do not themselves increase permeability, and mere heating of latex to 80° C for 10 minutes has practically no effect. The large increase in permeability must, therefore, be ascribed to a change in the structure of the film, due to vulcanization in the latex state. Vulcanization in the dry state does not bring about an increase, but usually a decrease in permeability. We believe that the large difference in the permeability of these vulcanized samples confirms the opinion expressed in a previous publication[7] that the structure of a latex film vulcanized in the dry state is considerably different from that of a film obtained from vulcanized latex, especially from vulcanized fresh latex. In another publication we shall give further data showing that it is possible to prepare rubber with low permeability to water vapor, even from vulcanized latex.

### (e) Plasticizing

The question was studied as to whether the effect of plasticizing* is still perceptible after vulcanizing rubber at a high temperature (147° C). The results of these tests are summarized in Table 6. The experiments were carried out by preparing, on the one hand, a mixture in the latex state and then drying it in the form of films at room temperature, and, on the other hand, by drying latex as such and mixing on a mill after plasticizing the whole rubber. The plasticized mixture was calendered to the same thickness as were the whole rubber films. Both rubbers were then vulcanized for different periods between plates under mechanical pressure in an autoclave. The results are summarized in Table 6; the state of vulcanization may be judged from the permanent set in ice-water, determined by the method of Fielding[8]. As a control of the permanent set, some sulfur determinations were made at the same time.

In view of the fact that series A vulcanized more slowly than series B, it is necessary to compare, for example, A, vulcanized 25 minutes, with B, vulcanized 20 minutes. The permeability constants of these samples were 10.0 and 7.2, respectively, so there was a significant difference between the two. Such a difference was found for the other degrees of vulcanization. Besides the permeability, the mechanical properties should be noted. It is evident that plasticizing produced greater stiffness and lower elasticity and

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* Plasticizing of crude rubber has an effect analogous to that of stretching. For an unvulcanized film from centrifuge cream, six months old, we found:
    Film as such, $P = 18.5$ (g. per cm. per hr. per mm. Hg $\times 10^{-3}$).
    After plasticizing and calendering, $P = 7.6$.

TABLE 6

EFFECT OF PLASTICIZATION ON THE PERMEABILITY CONSTANT OF RUBBER
Rubber used: whole-latex rubber from centrifuge cream, two days old, prepared from fresh field-latex.

A: mixture prepared in the latex state[a].
B: mixture prepared on a roll mill.

| Rubber | Time of vulcanization (min.) | Mechanical properties[d], at 0 and 79 per cent relative humidity, respectively | | | | | | Permanent set at 0° C (per cent) | $P^b$ (g. per cm. per hr. per mm. Hg $\times 10^{-8}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | Modulus at 600% elongation | | Tensile strength | | Elongation at break (per cent) | | | |
| A (not plasticized) | 15 | 68 | 28 | 322 | 249 | 918 | 968 | 480 | 8.8 |
| | 20 | 78 | 41 | 395 | 324 | 909 | 931 | 400 | 9.1 |
| | 25 | 90 | 51 | 386 | 328 | 880 | 888 | 25 [c] | 10.0 |
| | 30 | 89 | 59 | 367 | 308 | 856 | 841 | 20 | 10.3 |
| | 35 | 91 | 49 | 377 | 318 | 869 | 879 | 12 | 8.8 |
| | 40 | 80 | 49 | 375 | 325 | 892 | 878 | 4 | 7.9 |
| B (plasticized) | 15 | 36 | 30 | 292 | 231 | 912 | 867 | 366 | 7.8 |
| | 20 | 62 | 50 | 317 | 278 | 832 | 841 | 22 | 7.2 |
| | 25 | 82 | 54 | 340 | 323 | 816 | 834 | 11 [c] | 7.1 |
| | 30 | 117 | 76 | 332 | 330 | 774 | 815 | 5 | 7.4 |
| | 35 | 126 | 84 | 321 | 306 | 757 | 775 | 8 | 7.1 |
| | 40 | 126 | 91 | 336 | 314 | 759 | 777 | 5 | 7.1 |

[a] Composition: rubber 100; zinc oxide 3; sulfur 3; diphenylguanidine 1; vulcanized at 147° C.
[b] $p_1 - p_2 = 26.3$ mm. Hg; $p_2 = 0.0$ mm. Hg.  Thickness of the rubber $= 0.5$ mm.
[c] A: free sulfur 0.93; total sulfur 2.68.
   B: free sulfur 0.77; total sulfur 2.63.
[d] Test rods about 0.5 mm. think.

tensile strength in the corresponding vulcanized rubbers.  The tests were repeated several times, for instance with the mercaptobenzothiazole mixture of the American Chemical Society and with rubber from other latices; under these conditions, plasticizing rubber lowered its permeability constant in every case.  The less thoroughly the latex had been purified, the greater was the decrease in permeability.  At the same time an effect on the mechanical properties was observed, as in the example above.  We may conclude from this that in rubber which has not been plasticized, even though vulcanized at high temperature under mechanical pressure, the latex particles coalesce to a smaller extent than in rubber mixtures prepared on a roll mill.  The use of latex is, therefore, not recommended for the manufacture of articles which should have a low permeability to water vapor.

For the present we shall not offer an opinion as to whether vulcanized, plasticized rubber presents a continuous rubber phase, or whether it still contains individual or only partly coalesced latex particles.  But it should be mentioned that, according to Sebrell, Park and Martin[9], it is probable that even rubber obtained by drying a rubber solution always retains a structure derived from the original latex particles.  The same investigators are of the opinion that vulcanized rubber obtained from plasticized rubber has a discontinuous structure, which is attributable to incompletely coalesced latex particles.

## SUMMARY

The diffusion of water vapor through rubber films was measured by a simple method as a means of studying the structure of vulcanized and of unvulcanized rubber.  Dishes partly filled with water and sealed with rubber films were kept over silica gel, and the losses in weight were determined; the

mean error of the method was about 9 per cent. When desired, the water vapor diffusion was measured at different vapor tension values by placing saturated solutions of various salts in the dishes.

Experiments were made to ascertain to what extent the diffusion obeys Fick's law. Although there was a tendency for the diffusion constant to increase with the thickness of the rubber film, in agreement with the observations of Taylor, Hermann and Kemp[4], this relation could not be definitely established for rubber mixed on a roll mill (see Table 1) because of the limited accuracy of the method. In the case of latex films, a more pronounced but more irregular effect was observed (see Table 2). However, it is quite possible that the structure of a thicker latex film is different from that of a thinner one, so it is doubtful to what the effect observed should be attributed. Therefore, since no real diffusion constant is involved, the value which still must be calculated to compare results is termed the *permeability constant, P*. Because of the effect of the thickness of the film, we endeavored in all cases to make the measurements with films 0.5 mm. thick; a variation greater than between 0.4 and 0.6 mm. was not permitted. In carrying out the measurements at different vapor pressure differentials, we found that the law of Fick was in general not followed. The deviation was considerable in the case of unvulcanized latex films (see Table 3). Vulcanized rubber, mixed on a roll mill, showed diffusion in fair agreement with Fick's law; the permeability constant increased only when the vapor pressure differential was high (see also IV). Vulcanized latex films occupied in this respect a position between the unvulcanized latex film and the vulcanized rubber mixed on a roll mill. $P$ must, therefore, be characterized not only by the thickness of the film but also by the vapor pressure differential. Most measurements were made at a vapor pressure differential of 26.3 mm. Hg (28° C).

Salts added to latex had little or no effect on the permeability constant for water vapor of unvulcanized rubber films prepared from this latex. The addition of zinc oxide and sulfur also made practically no difference.

However, when the composition or size of the adsorption layer on the latex particles was altered by the addition of certain substances to the latex, a considerable change in permeability resulted. Thus the permeability was increased by alkalies because they hydrolyzed the proteins in the latex. Casein and saponin also increased the permeability; saponin had a pronounced effect, particularly when the latex had not been purified, whereas the influence of casein was more noticeable with purified latex.

The permeability constant was not affected when the rubber was dried or absorbed moisture. Heating or stretching of unvulcanized rubber led to a decrease in permeability. This effect was the greater the higher the permeability of the film that had not been thus pretreated (see Table 4). This was particularly noticeable with films containing saponin. It follows from these observations that the latex particles in a latex film dried at room temperature are still present as separate units, and that the diffusion of water vapor takes place principally through the continuous structure of the adsorption films. This structure is destroyed by stretching or heating, and is replaced by a continuous rubber structure which is much less permeable. Latex films that have been vulcanized at a temperature of 90° C or higher do not exhibit these phenomena, or do so only to a much lesser degree if the latex particles during the vulcanization have not completely coalesced. Rubber from vulcanized latex and films vulcanized in the dry state at a lower temperature are affected by heating in about the same way.

Plasticization of an unvulcanized latex film, followed by calendering to the original thickness, also decreased the permeability.

When latex was stored, the permeability of rubber films prepared from it increased, no matter whether it was vulcanized or not.    To obtain latex rubber with a low permeability to water vapor, it is necessary always to choose a latex that has been purified as short a time as possible before use (see Table 5).

Vulcanization in the latex state usually yields rubber with a very high permeability; this is especially true of fresh latex (see Table 5).    There is, therefore, a considerable structural difference between latex films that have been vulcanized in the dry state at a high temperature, and those prepared from vulcanized latex.    In rubber from vulcanized latex, the latex particles showed, as a rule, less coalescence than in an unvulcanized latex film[7].

The effect of plasticizing was investigated by preparing a mixture of the same composition, in the latex state on the one hand, and on a roll mill with whole rubber from this latex on the other hand.    The two mixtures were then vulcanized in exactly the same way (see Table 6).    The permeability of the plasticized rubber was lower than that of the unplasticized mixture.    In spite of vulcanization at a high temperature, and in spite of mechanical pressure applied during vulcanization, the unplasticized vulcanized rubber did not show an ideal continuous rubber structure.    It was found also in these experiments that plasticized rubber, at the same degree of vulcanization, was stiffer and at the same time was of lower elasticity and lower breaking strength.    The question whether this is to be attributed to differences in microstructure or molecular structure must for the present be left unanswered.

The results show that measurement of permeability to water vapor may be used as an important aid in securing an insight into the microstructure of both vulcanized and unvulcanized rubber.

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# VIBRATION PROPERTIES OF RUBBERLIKE MATERIALS

## DEPENDENCE ON TEMPERATURE *

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The dynamic properties of rubber or rubber substitutes, when used as anti-vibration material, are of importance to the engineer because they predict the actual performance of the material when in use and may differ greatly from the static values. They are also important to the compounder because of their sensitiveness to compounding changes and because of the facility with which tests may be made under widely different conditions. Finally, they are of interest to the scientist because they throw new light on the complex problem of the molecular structure of these materials.

Many methods for obtaining the dynamic properties have been described in recent literature. In particular, papers by Sebrell and Dinsmore[1] and Gehman, Woodford, and Stambaugh[2] describe a vibrator, developed at The Goodyear Tire & Rubber Company, by means of which the dynamic modulus and internal friction of rubber can be determined. The present paper describes additional measurements, made with this machine, of the effects of frequency and temperature on the properties of rubber and some synthetic materials. Details of the construction and theory of the vibrator and a complete list of references are given in these papers[3].

## VIBRATOR

The Goodyear vibrator (Figure 1) consists of a rebuilt loud-speaker unit, the moving coil of which is fastened to a yoke holding the rubber samples. The test-pieces are two $\frac{1}{2} \times \frac{1}{2}$ inch cylindrical samples, mounted one on either side of the vibrating yoke, as shown in Figure 2. They may be placed under any desired static compression by adjusting the supporting frame which is fastened rigidly to the loud-speaker magnet. By means of an audio oscillator and a 100-watt amplifier, the samples may be made to vibrate at various frequencies and amplitudes.

By clamping weights to the brass rod connecting the moving coil to the yoke, the mass of the vibrating system, and hence its resonant frequency, may be adjusted.

The dynamic modulus is obtained by adjusting the mass until the maximum amplitude (resonance) is obtained at the desired frequency. Then the modulus, $E$, is given by the formula:

$$E = Mq\omega^2 \text{ dynes per sq. cm.}$$

where $M$ = mass (grams)

$q$ = a shape constant = $\frac{1}{2} \left( \frac{\text{height}}{\text{area}} \right)$ = 0.501 cm.$^{-1}$

$\omega$ = frequency, in radians per sec., or $2\pi \times$ frequency, $\nu$, in cycles per sec.
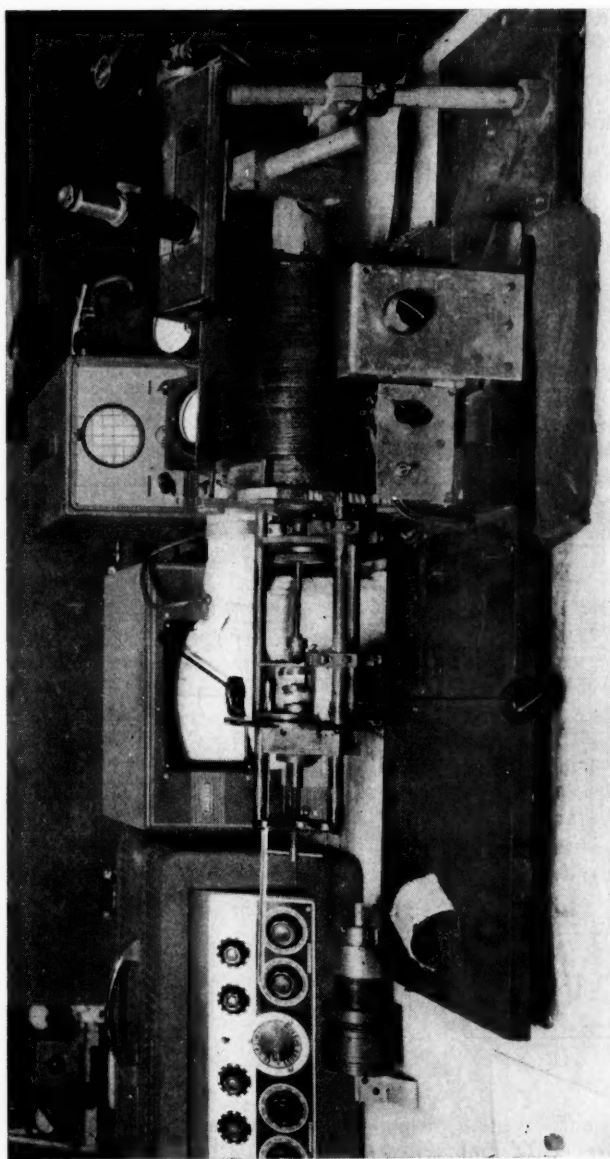
FIG. 1.—Photograph of apparatus.

thus:

$$E = 2.02 \times 10^{-6} M\nu^2 \text{kg. per sq. cm.}$$

The internal friction, $\eta$, is calculated from the maximum amplitude at resonance by means of the formula:

$$\eta = Fq/x\omega \text{ c.g.s. units (poises)}$$

where $F$ = driving force (in dynes) proportional to current in moving coil
$x$ = amplitude (cm.)
Hence, for the particular field magnet and coil of this vibrator:

$$\eta = 54,100 \, i/x\nu$$

where $i$ = driving current, root mean square amperes
Dynamic resilience is obtained by substituting in the expression:

$$R = 100e^{-(4\pi^2\nu\eta/E)}\%$$

To raise the temperature of the samples above that of the room, the sample holder was enclosed in a simple oven. A stream of air, of adjustable pressure, passes over a heating unit and past a thermoswitch before flowing into the insulated chamber surrounding the rubber samples (Figure 2). The air flows
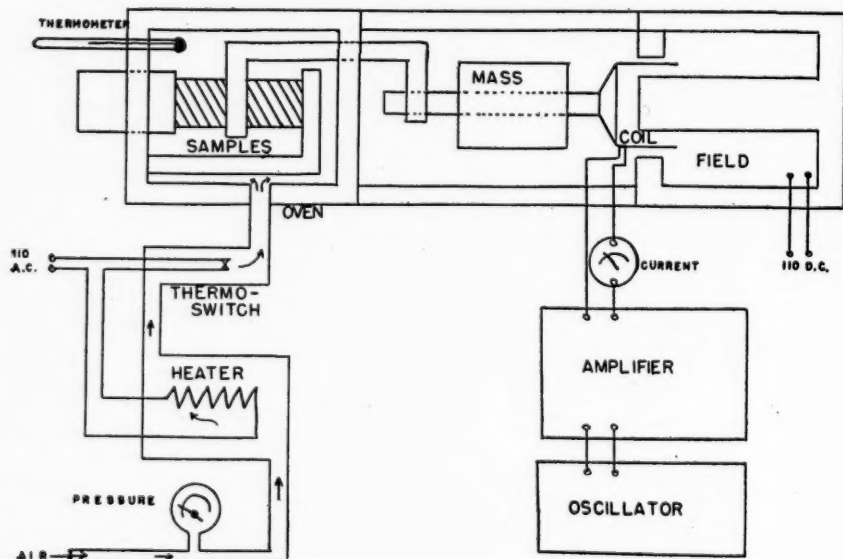


Fig. 2.—Diagram of apparatus.

out through small holes at various parts of the enclosure, so that there are no dead-air spaces. For high temperatures, heat losses by conduction through the metal framework are reduced by heating the sample holder by means of two soldering-iron heating elements inserted in holes in the frame.

The thermostatic control keeps the temperature of the air surrounding the sample constant within 0.5° C, measured by a mercury thermometer. The temperature of the samples is measured with a needle thermocouple, and is

within 1–3° C of that indicated by the mercury thermometer, if sufficient time has been given for thermal equilibrium.

To get temperatures below that of the room, the air is passsed through a drying tube and through a copper coil immersed in a solution of solid carbon dioxide in acetone, and then directly into the chamber around the samples. Since there is no thermostatic control, the temperature is controlled by manually adjusting the rate of air flow.

The thermocouple was made by passing a fine, insulated constantan wire through a steel hypodermic needle, soldering, and then sharpening the point. The thermal e.m.f. developed when the needle was inserted into a rubber sample was measured by a Leeds & Northrup compensated temperature indicator with special calibration.

### PROCEDURE AND STOCKS TESTED

Eight $\frac{1}{2} \times \frac{1}{2}$ inch cylindrical samples of the stock were moulded and numbered. Samples 1 and 2 were placed in the vibrator under a static compression of 12 per cent and tested at room temperature at a low amplitude, so that the heat generation was not appreciable. By varying the mass of the vibrating system, a series of measurements was made over a frequency range of about 30 to 90 cycles per second. The vibrator was on such a short time for each reading that the heating or fatigue of the sample was negligible. The thermostat was then set for about 35° C, and the air stream turned on. After allowing 30 minutes or more for temperature equilibrium, the vibrator was turned on, and another reading made at 60 cycles per second. The temperature of sample 1 was measured by inserting the needle thermocouple into its center. This punctured sample was then removed, sample 3 was placed in the vibrator with sample 2, and the thermostat was set for about 10° C higher. This procedure was repeated, putting in a fresh sample to replace the punctured one each time, until samples 7 and 8 were measured at about 110° C. These samples were tested over the entire frequency range before the temperature was measured.

In the same manner, the vibration properties of several stocks were measured at low temperatures, beginning at room temperature and decreasing the temperature after each test by increasing the flow of cold air into the sample chamber. The natural and synthetic stocks tested are listed in Table I, with the compounding ingredients and cures.

### TABLE I
#### CURES AND COMPOSITIONS OF STOCKS

| Stock | Cure | | Poly-mer | Gas black | Sul-fur | Zinc oxide | Stearic acid | Accel-erator | Anti-oxi-dant | Plasti-cizer |
|-------|------|------|------|------|------|------|------|------|------|------|
| | (min.) | (° F.) | | | | | | | | |
| Natural rubber gum stock | 65 | 260 | 100 | 0 | 3 | 5 | 3 | 0.5 | 1 | .. |
| Natural rubber | 55 | 260 | 100 | 42.6 | 3 | 5 | 3 | 1 | .. | .. |
| Synthetic A | 50 | 260 | 110 | 40 | 1.6 | 5 | 2 | 1 | .. | .. |
| Synthetic B | 50 | 260 | 103 | 40 | 1.6 | 5 | 2 | 1 | .. | .. |
| Synthetic C | 50 | 260 | 103 | 40 | 1.6 | 5 | 2 | 1 | .. | .. |
| Synthetic D | 85 | 260 | 103 | 40 | 1.6 | 5 | 2 | 1 | .. | .. |
| Synthetic E | 70 | 260 | 103 | 40 | 1.6 | 5 | 2 | 1 | .. | .. |
| Thiokol | 60 | 290 | 100 | 29 | ... | 5 | 1 | 0.45 | .. | .. |
| Neoprene-E | 15 | 290 | 102 | 31.8 | ... | 5 | 2 | 4 | 2 | 0.25 |
| Neoprene-GN | 30 | 290 | 102 | 32 | ... | 5 | 2 | 4 | 2 | 0.25 |
| Buna-N (Stanco Distributors) | 45 | 260 | 103 | 40 | 1.6 | 5 | 2 | 1.35 | .. | .. |

The accelerator used for the Neoprene stocks was magnesia; for Thiokol, 0.35 part of Altax and 0.10 part of D.P.G.; for the gum stock, Captax; and for all the others, a special Captax derivative, except for the Standard Oil Buna, which contained 0.35 part of Altax also. The antioxidant used for the gum stock was phenyl-$\beta$-naphthylamine, and for the Neoprenes, Neozone-A. The Neoprenes also contained Latac as plasticizer.

Synthetic stocks A, B, and C were made from different butadiene-acrylonitrile copolymers. Synthetics D and E were butadiene-styrene copolymers.

## DATA

Table II is a summary of the vibration properties at room temperature (28° C) and 60 cycles per second. For comparison, the pendulum rebound is given wherever such data were available. As explained previously[2], the dynamic resilience should be related to the square of the rebound values.

TABLE II

VIBRATION PROPERTIES AT 28° C AND 60 CYCLES PER SECOND

| Stock | Dynamic modulus (kg. per sq. cm.) | Internal friction (c.g.s. × $10^{-2}$) | Resilience (percentage) | Rebound (percentage) | $Hx$ at 28° C. | $Hx$ at 100° C. | $\Delta T$ ° C. | Flexometer Relative $\Delta T$ |
|---|---|---|---|---|---|---|---|---|
| Natural-rubber gum stock | . 29 | 3.0 | 78 | .. | 13.6 | 18 | 6 | 8.5 |
| Natural rubber | 98 | 26.5 | 52 | 72 | 100 | 100 | 71 | 100 |
| Synthetic A | 225 | 107 | 32 | 53 | 312 | 222 | 113 | 160 |
| Synthetic B | 198 | 102 | 29 | 51.5 | 298 | 210 | 107 | 151 |
| Synthetic C | 572 | 347 | 23 | 31 | 936 | 374 | 133 | 187 |
| Synthetic D | 171 | 85 | 30 | 54 | 326 | 164 | 102 | 144 |
| Synthetic E | 100 | 135 | 16.5 | .. | 321 | 154 | ... | ... |
| Thiokol | 145 | 64 | 34.5 | 56 | 202 | 87 | ... | ... |
| Neoprene-E | 127 | 50.5 | 38 | 65 | 167 | 168 | 97 | 136 |
| Neoprene-GN | 144 | 48 | 45 | 60 | 169 | 190 | 115 | 162 |
| Standard-Oil Buna | 149 | 78 | 28 | 56 | 228 | 175 | ... | ... |

From the vibration measurements, the relative rates of heat generation can be calculated. The heat generation at constant amplitude, $Hx$, should be proportional to $(100 - R)Ex^2$, where $R$ is resilience, $E$ is modulus, and $x$ is amplitude. Since $R$ and $E$ are functions of temperature, the value of $Hx$ calculated for room temperature does not always agree with the measured temperature rise. The calculated values for $Hx$, based on the properties at 100° C, are given in Table II, along with the actual temperature rise of samples of the same stocks subjected to 15 minutes vibration in the Goodyear Flexometer (The Goodyear Flexometer is a large electric vibrator, similar to the small vibrator. It operates at 60 cycles per second, and at any desired constant amplitude. Temperatures are measured with the needle thermocouple).

The value of $Hx$ for rubber was arbitrarily set at 100, and the other values were rated accordingly. It is evident that the relative heat generation rates, calculated from room temperature values of the dynamic modulus and resilience, in some cases are not proportional to the observed temperature rises. As is to be expected, the agreement is very much improved when the relative heat generation rates are calculated from dynamic values measured at 100° C.

The higher temperatures developed in the Flexometer, as well as the heat losses which are not considered in calculating $Hx$, are sufficient to explain the differences.

## EFFECT OF FREQUENCY

Figure 3 shows the dependence of modulus on frequency at room temperature, and Figure 4, at 110° C.   In most cases the modulus is not affected by frequency, although there appears to be a slight effect in the case of Neoprene E.   In Figure 4 Neoprene E, synthetic A, and rubber show a small decrease in modulus with increasing frequency.   This effect is probably due to the increase in heat generation at higher frequencies since, at constant amplitude, heat generation is proportional to frequency.   The amplitude was purposely kept low to minimize this effect.

There is considerable scattering of the points for some stocks, especially synthetic A, which is due to the high internal friction.   This tends to make a broad resonance curve so that it is difficult to observe the exact resonant frequency.   The independence of the modulus of frequency has been noted by Gehman et al.[4], Kosten[5], and others.   Naunton and Waring[6], on the other hand, found a large increase in modulus with frequency, especially for heavily loaded stocks.   Possibly this was due to a decrease in amplitude of vibration at higher frequencies, or it may have been a result of the high range of frequencies studied (80 to 1000 cycles per second).

Figures 5 and 6 show the variation of internal friction with frequency. In general, friction is nearly inversely proportional to frequency.   For instance, the curve for natural rubber is not drawn through the points but, instead, fits the equation:

$$\text{internal friction } (\eta) \times \text{frequency } (\nu) = 1720$$
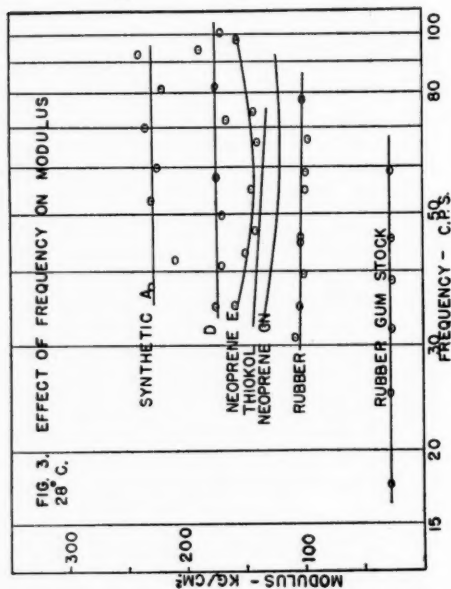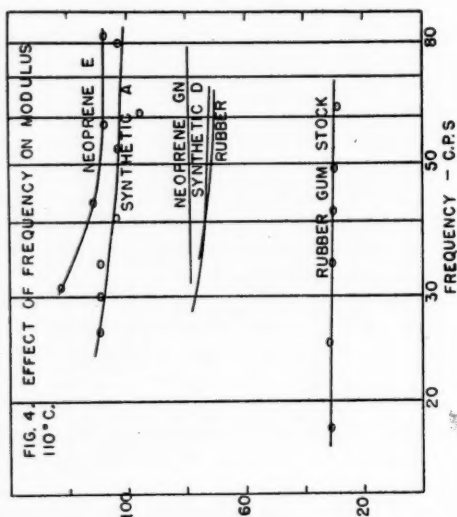
The dotted line near the curve for synthetic D is drawn to fit the equation: $\eta\nu = 5330$.   Similarly, the dotted curve in Figure 6 is drawn to fit: $\eta\nu = 890$. The friction usually falls off too fast as the frequency is raised for a perfect fit with the theoretical curve, except for the gum stock.   This effect is very noticeable for synthetic C at 110° C.   This stock had too high a modulus and friction to be plotted in the other figures.
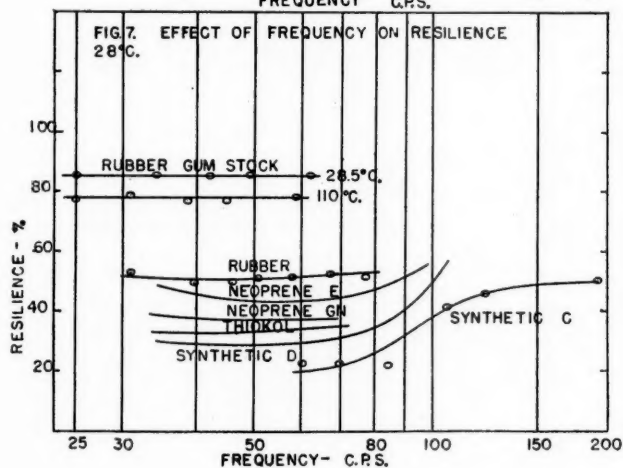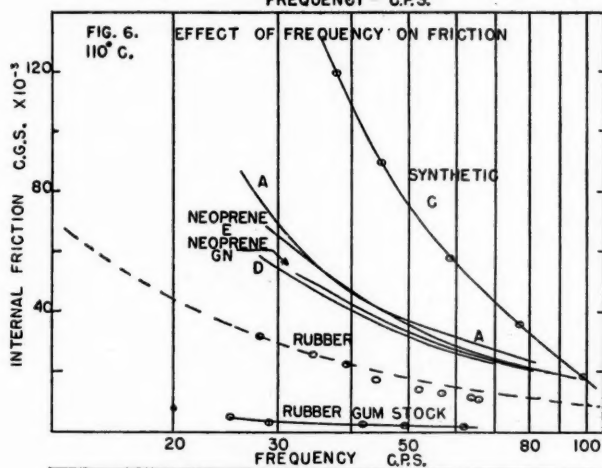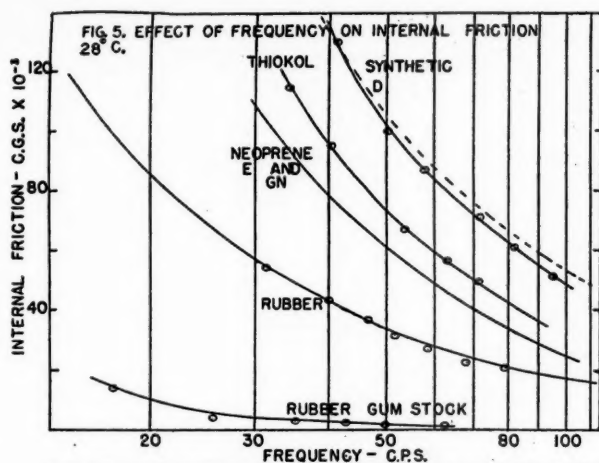
In the usually assumed equation of motion for vibrating systems, the internal friction, like viscosity, is supposed to be independent of frequency. However, most observers have reported a nearly hyperbolic relation.   Kimball[7] discussed this problem of solid friction.   It is obvious that vibration friction must decrease with frequency; otherwise a steel bell would not ring when struck, but would give a dull thud, like a lead or clay bell.

The deviations from the hyperbolic relation shown in Figures 5 and 6 may be explained by an additional decrease in friction as a result of the greater heat generation at higher frequencies.   This effect can also be noted in Figure 7. If the product $\nu \times \eta \times (1/E)$ were constant with frequency, the dynamic resilience should also be constant.   However, there is a pronounced rise in the curves for Neoprene-E and synthetics C and D.

## EFFECT OF TEMPERATURE ON MODULUS

When rubber is stretched, the increase in modulus with temperature is well known.   This property has been explained (for instance, by Mark[8]) as due to the increase in thermal energy of the oriented molecules, which increases the force tending to restore them to their normal random arrangements.   This effect, therefore, should be noticeable only when the distortion of the sample is great enough to cause a considerable orientation of the molecules.   In the case of small stresses, such as are found in static compression applied to the

FIG. 3.  EFFECT OF FREQUENCY ON MODULUS
28° C.

FIG. 4.  EFFECT OF FREQUENCY ON MODULUS
110° C.

FIG. 5. EFFECT OF FREQUENCY ON INTERNAL FRICTION 28° C.



FIG. 6. EFFECT OF FREQUENCY ON FRICTION 110° C.



FIG. 7. EFFECT OF FREQUENCY ON RESILIENCE 28°C.

samples in the vibrator, the effect should be masked by the normal decrease in modulus shown by ordinary solids.

In Figure 8 a large decrease in modulus with temperature is apparent. This was also observed by Gehman[9] at a comparatively low frequency. It is

FIG. 8. EFFECT OF TEMPERATURE ON MODULUS 60 C.P.S.

FIG. 9. EFFECT OF TEMPERATURE ON RESILIENCE 60 C.P.S.
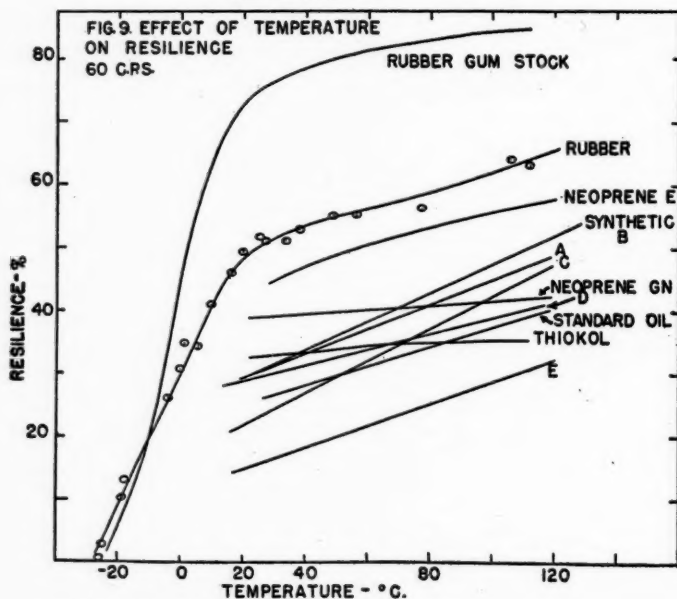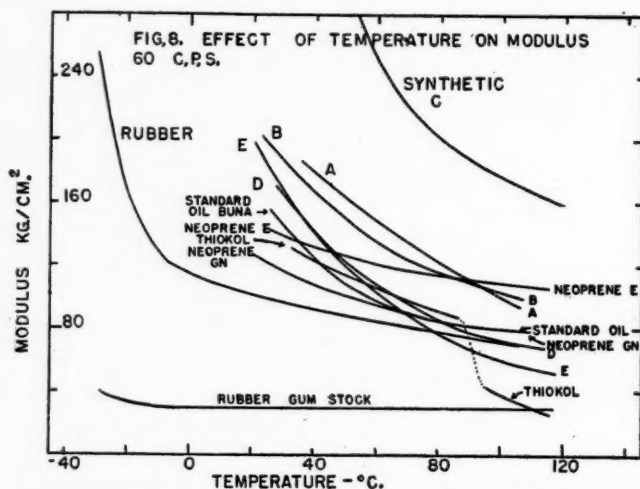
interesting to note that the gum stock was not softened by temperature above about 0° C. As a matter of fact, a slight increase was noted, but this was probably due to an increase in the percentage compression of the sample resulting from thermal expansion.

Although synthetic C is much harder than any of the other stocks, the shape of the curve is not very different.    At lower temperatures, rubber becomes just as stiff as the synthetic stocks.

The Thiokol sample shows a sharp decrease in modulus and friction (Figure 10) at about 90° C, which might be called a "melting point".    The stock



FIG. 10. EFFECT OF TEMP. ON FRICTION 60 C.P.S.



FIG. 11. EFFECT OF TEMP ON FRICTION 60 C.P.S.
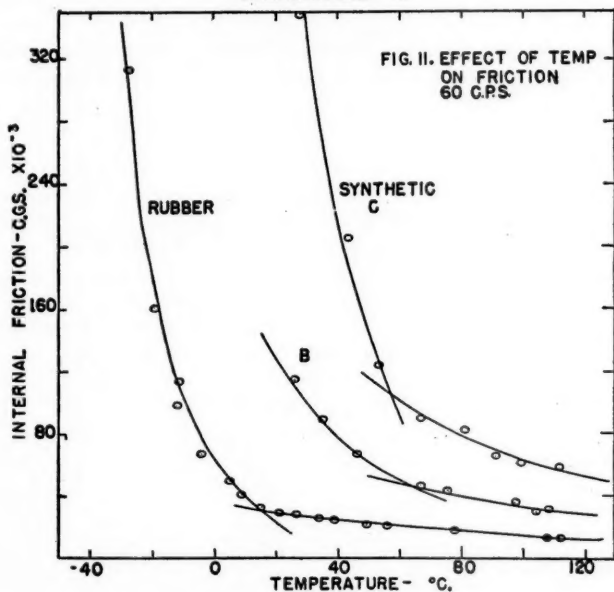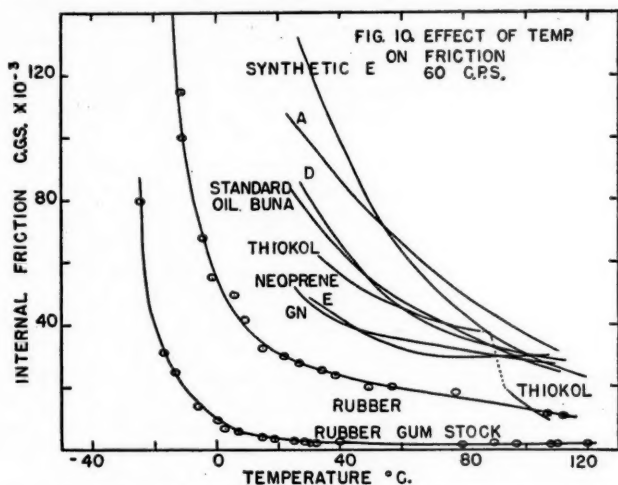
became soft and sticky, with a high plastic flow.    For this reason the effect of frequency could not be checked at the high temperature.    A permanent deformation remained after removal from the vibrator.    Since both the modulus and friction were decreased in the same proportion, the resilience does not show any sudden change at this point (Figure 9).

## EFFECT OF TEMPERATURE ON FRICTION

The change in internal friction with temperature is illustrated in Figures 10 and 11. As the temperature is raised from low values, the friction falls rapidly at first, and then nearly levels off at high temperatures. The resilience (Figure 9) rises almost linearly with temperature above 30° C. Below this point, for rubber at least, a fairly sudden transition occurs, and the resilience falls rapidly with a further decrease in temperature. It is possible that the resilience of the other stocks would show similar behavior, but the modulus and friction became so high that the vibrator results could not be depended upon. Roelig[10] also shows a linear rise of resilience (or fall of percentage damping) with temperature.

Although stretched rubber has sometimes been compared with a gas because of the rise of modulus with temperature, these measurements have shown that, in compression at least, the material may be considered a normal solid insofar as the behavior of the modulus as frequency and temperature are varied. The internal friction also is more like that of a solid than like the viscosity of a liquid, because of its hyperbolic relation with frequency. However, there is a striking similarity to liquids in the effect of temperature on internal friction.

The viscosity of a liquid is usually assumed to depend exponentially on the reciprocal of the absolute temperature. According to Ward[11], when a shearing stress is placed on a liquid, a configuration change results which requires a certain amount of energy, $B$. The number of molecules with this amount of energy is given by the Boltzmann equation as proportional to exponent $(-B/T)$, where $T$ is the absolute temperature. The viscosity, $\eta$, is inversely proportional to the number of molecules containing sufficient energy to bring about the configuration change necessary to relax the shearing stress:

$$1/\eta = A e^{-B/T} \tag{1}$$

It is probable that both $A$ and $B$ are functions of temperature also, but they are difficult to evaluate accurately so their deviations with temperature are usually obtained from the data when variations from the simple formula are found. Smallwood[12] applied this formula to the plastic flow of raw rubber. Three stocks were chosen to check the application of this formula to the vibration friction of rubberlike materials. The data for rubber and synthetics B and C are plotted in Figure 11. The curves were drawn, according to Equation 1 for $\eta$, to fit the data as closely as possible. It is apparent that two curves are necessary to describe each of the three stocks. The low-temperature high-friction part of the data falls on a theoretical curve, $\eta = A_1 e^{B_1/T}$; the high-temperature low-friction data fall on another curve, $\eta = A_2 e^{B_2/T}$. The values of these constants follow:

| Stock | $A_1$ | $B_1$ | $A_2$ | $B_2$ |
|---|---|---|---|---|
| Rubber | 0.15 | 3550 | 875 | 1032 |
| Synthetic B | 45.7 | 2325 | 1350 | 1190 |
| Synthetic C | 0.191 | 4375 | 1020 | 1540 |

Thus it appears that $A$ and $B$ suddenly change as the temperature rises. This can be seen more clearly on Figure 12, where the natural logarithm of $\eta$ is plotted against the reciprocal of the absolute temperature. On this plot the ideal liquid would give a straight line. The data for each of these stocks fall on two straight lines, with a sharp transition at a critical temperature.

FIG. 13. RESONANCE CURVES FOR TREAD STOCK



FIG. 12. LOG$_e$ $\eta$ VS $1/T°A$
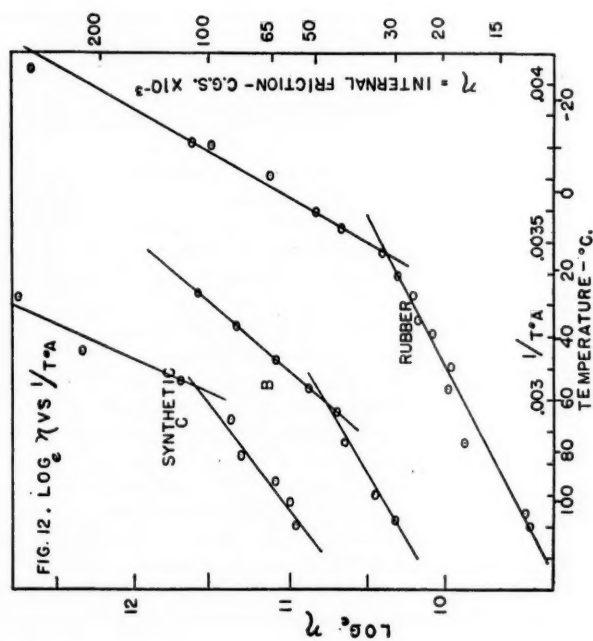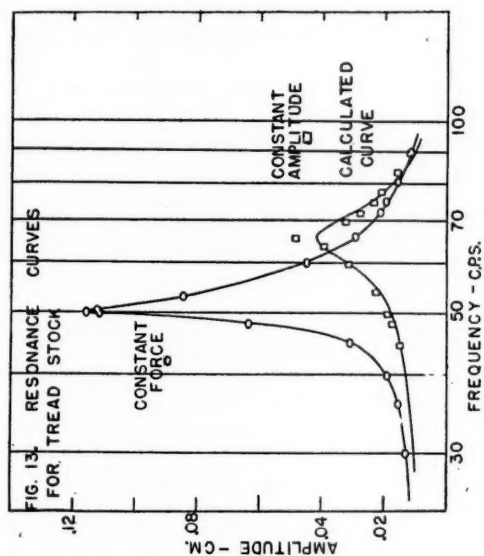
From x-ray studies of liquids, it has been found that the structure can be represented by an average configuration of the molecules in more or less ordered groups.    The thermal energy is too great for the molecules to be bound into any definite crystal lattice but, on the average, this semblance of order appears. $B$ was defined above as the molecular energy necessary for a change in configuration to result from an applied stress.    For a given average configuration, $B$ should be almost independent of temperature.    If some change in the configuration is produced by the temperature change, $B$ will change also.    For example, suppose that, at a particular temperature, the thermal energy given to an angular vibration in the molecules of a liquid becomes great enough to permit free rotation.    At this point the cohesive forces holding the molecules in their average relative positions undergo some revisions, and a decrease in $B$ should result.
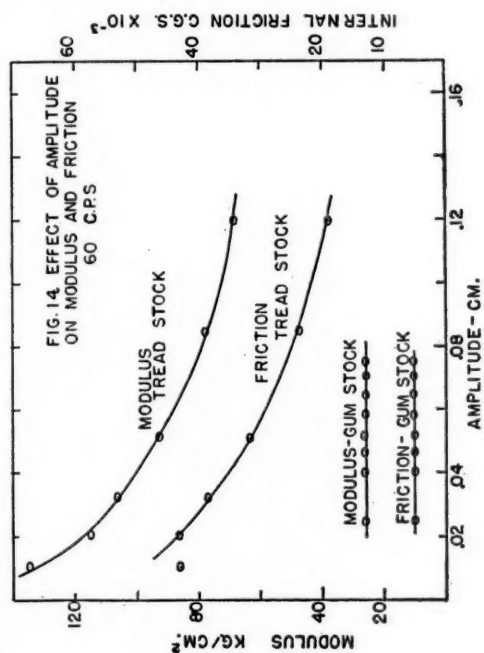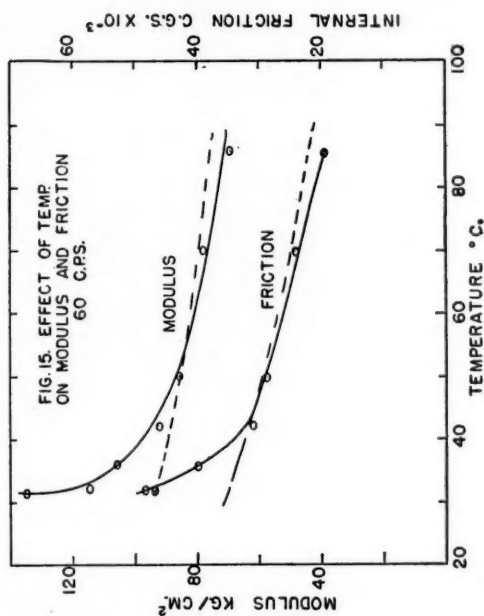
It seems possible that this same explanation will fit the case of rubber and similar long-chain elastic materials.    Possibly the sharp breaks in the $\ln \eta$ vs. $1/T$ plots indicate the temperature at which some secondary bond is broken, lowering the potential barrier required for a configurational change and permitting a relative motion along the molecules or parts of molecules with less applied energy.    A more thorough investigation of this change in $B$ may lead to some important clues as to the true structure of these materials.
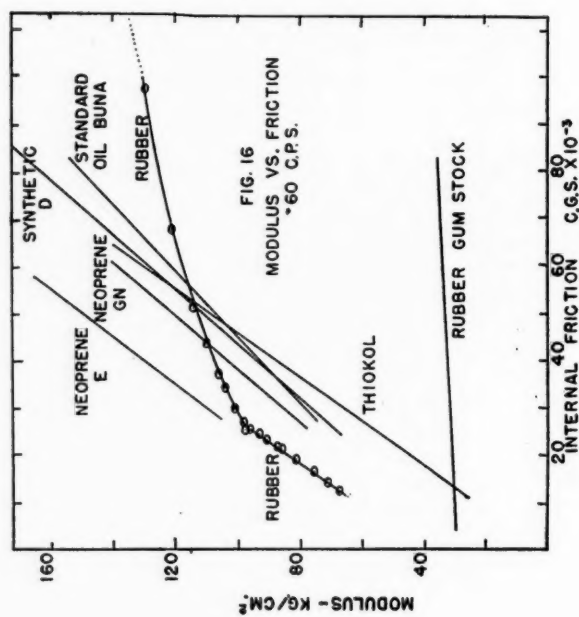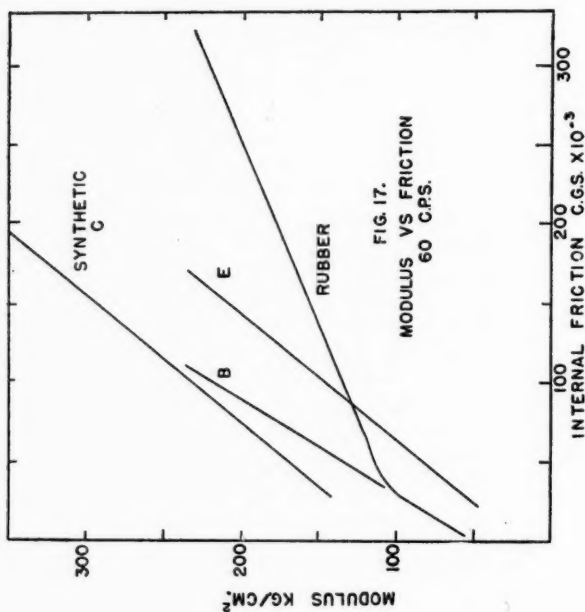
## EFFECT OF AMPLITUDE

Almost every observer of the vibration properties of loaded rubber stocks and other materials has noted the effect of the amplitude of vibration on the modulus and internal friction[13].    As stated by Gehman[9], the obvious explanation that the reduction of these properties with increasing amplitude is caused by a temperature rise of the sample due to heat generated in it is not completely satisfactory, as there should be a lowering of modulus with frequency which is not found.    Furthermore, the effect is noticed at very small amplitudes which could not generate sufficient heat to raise the temperature more than a few degrees.

To investigate this effect, a sample of a standard tread stock was used which was similar to the natural rubber sample for which measurements have been given except that it was loaded with about 50 parts of gas black instead of 40.    A resonance curve was obtained by holding the mass constant at 1290 grams, varying the frequency, and adjusting the driving force to keep the amplitude nearly constant.    The values of current thus obtained were divided into the amplitudes to give an amplitude-frequency curve in which the effect of amplitude was almost absent.    These are plotted as squares in Figure 13. On account of limitations of the measuring equipment, the amplitude at the resonant frequency was slightly larger than for other parts of the curve.    This probably accounts for the deviation from the calculated curve, drawn to represent an ideal stock of modulus equal to 113.2 kg. per sq. cm. and a friction of 59,000 c.g.s. units.    The other curve of Figure 13 was obtained by the ordinary method of holding the driving force constant, and observing the amplitude.    The curves are adjusted to the same driving force.    This shows what an enormous effect the amplitude of vibration has on the properties of a loaded stock.    The natural rubber gum stock showed no effects due to amplitude over the range tested, and the data agreed closely with the calculated curve.

Figure 14 shows the effect of the amplitude on the modulus and friction for both tread stock and gum stock at 60 cycles per second.    At each ampli-

FIG.15. EFFECT OF TEMP.
ON MODULUS AND FRICTION
60 C.P.S.

FIG.14. EFFECT OF AMPLITUDE
ON MODULUS AND FRICTION
60 C.P.S

FIG. 16. MODULUS VS. FRICTION ·60 C.P.S.



FIG. 17. MODULUS VS FRICTION 60 C.P.S.

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tude a measurement of the temperature of the sample was made, using the needle thermocouple. From these data (Figure 15), the variation of modulus and friction is plotted against the temperature of the tread stock sample. The dotted lines represent the actual effect of temperature on the dynamic properties, obtained at a constant amplitude by means of the heating chamber. This shows clearly that temperature alone cannot account for the change in properties with the amplitude. The exact mechanism of this effect is not clear, although Lazan[14], working with metals and plastics, explains it as due to the nonlinearity of the stress-strain curves.

## INTERDEPENDENCE OF MODULUS AND FRICTION

A liquid has no elastic modulus (except compressibility). The viscosity is an inverse measure of the rate of flow produced by a given force. An ideal crystal, on the other hand, has no viscosity (below the elastic limit), and the modulus is a measure of the distortion produced by a given force. Rubber and similar materials have both a modulus and a sort of viscosity. The structure is not crystalline (except under special conditions) because it does not repeat itself again and again; however, there is apparently some rudimentary order in the molecular configuration, undoubtedly of a statistical nature, which is reassumed, approximately at least, after the distorting force is removed. This gives rise to a modulus. The distortion produced by the force may be so large that considerable relative motion of the molecules must take place. Many secondary bonds are broken and heat is generated. Thus, there is also internal friction or "viscosity".

Since both of these quantities are functions of the internal energy of the material, it is not surprising that they appear to be affected by temperature in the same manner.

In Figure 16, modulus is plotted against internal friction at 60 cycles per second over the temperature range studied. Even where there is considerable scattering of the points in other plots, the data fall in straight lines on this graph. This is good evidence that there is only one fundamental constant (for a given frequency) from which the internal friction and the modulus may be obtained. Gehman[9] also found this to be true for variations of apparent modulus and internal friction due to changes in the shape of the sample, and Gehman, Woodford, and Stambaugh[2] showed that $E$ and $\eta$ have a linear interdependence for different pigment loadings. Gemant[15] discussed a general molecular theory predicting this relation.

Figure 17 is plotted on a smaller scale to permit all of the data for synthetics B and E and natural rubber and most of the data for synthetic C to be represented. Natural rubber appears to be the only stock which requires two straight lines for representation. The junction of these two lines occurs at about 25° C, or about 8° higher than it occurred in Figure 12.

## CONCLUSIONS

1. The vibration modulus and resilience are independent of the frequency of vibration if the temperature is constant.

2. The internal friction is approximately inversely proportional to the frequency.

3. The modulus decreases as temperature increases. Curves for synthetic stocks at high temperatures are not very different from those of rubber at low temperatures.

4. Resilience rises linearly with temperature.   Rubber shows a transition from one slope to another at about 25° C.

5. The dependence of the internal friction of rubber and similar materials on temperature follows the same exponential law as the viscosity of liquids. At certain critical temperatures sudden changes occur in the cohesive forces, which cause a transition from one curve to another.   For the natural rubber sample this occurs at about 17° C.

6. The amplitude of vibration has a large inverse effect on the modulus and friction, which cannot be explained by the temperature rise of the sample due to heat generated in it.   The effect may be due to nonlinearity of the stress-strain curves.

7. Modulus and friction are affected by temperature in the same way, indicating the dependence of both on some fundamental characteristic of the molecular structure.   Natural rubber requires two straight lines for representation on the modulus-friction plot, the junction occurring at about 25° C.

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# NATURAL AGING OF RECLAIMED RUBBER *

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With the increasingly important role being played by reclaimed rubber in the war effort, it seems desirable to examine this raw material more closely than heretofore from the standpoint of maintenance of quality during natural aging. Some lots of reclaimed rubber in certain consumers' plants have attained greater age than usual because of unforeseen changes in production schedules, occasioned by the present situation. Moreover, the creation of a stock pile of reclaimed rubber from excess production, as an emergency supply, has been and may again be considered by the Government. Also, substantial amounts of reclaimed rubber have been exported and thereby have acquired more age than usual before use. Finally, certain manufacturers have desired that reclaimed rubber have a definite age from the standpoint of processing advantages; in some cases, an age of six months has been requested if possible.

Reclaimed rubber undergoes certain changes on aging. It becomes drier, nervier, and less tacky on the mill, and requires more mastication to achieve the desired workability. Palmer and Kilbourne[1] commented on this tendency, and showed that these changes are accompanied by a reduction in the chloroform extract of the reclaim. The purpose of this paper is to show the effect of these changes in properties of reclaimed rubber during aging on the quality of products in which it is used.

## PERIODIC TESTING OF DIFFERENT TYPES OF RECLAIM

Approximately one ton of each of three commercial products (Table I) was set aside from regular production. Five slabs of each reclaim were chosen,

TABLE I

ANALYSES OF RECLAIMS

| Reclaim Type | A Black passenger inner tube | B Black passenger inner tube | C Whole tire Blend of alkali digestion and open-steam |
|---|---|---|---|
| Mfg. process | Open-steam pan | Alkali digestion | |
| Analysis[a] (percentages) | | | |
| Acetone extract | 7.32 | 6.37 | 8.87 |
| Ash | 26.32 | 22.37 | 18.67 |
| Alkalinity | 0.79 | 0.14 | 0.09 |
| Total sulfur | 1.66 | 1.75 | 1.91 |
| Carbon black | 5.70 | 4.67 | 14.55 |
| Rubber content (by difference) | 59.00 | 64.84 | 56.00 |
| Specific gravity | 1.17 | 1.12 | 1.18 |

[a] Tests run when reclaims were two weeks old.

and samples obtained by cutting a strip across the cut end of each slab so that the entire cross-section of the slab was included. These five strips were blended before testing to make one composite and representative sample of

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each reclaim. The same five slabs of each reclaim were periodically tested as they increased in age.

Acetone extracts and chloroform (uncured) extracts were obtained by the method of Palmer and Kilbourne[1]. Milling tests were made by the procedure suggested by Palmer, Miller, and Brothers[2] and later described in detail by Palmer and Kilbourne[1]. It consists in milling a sample of the reclaim on a laboratory-size mill under standardized conditions with respect to batch size, roll temperature, roll speed, and roll setting. The times necessary for the reclaim to knit to the slow roll, reach a definite degree of smoothness, and leave the slow roll and adhere to the fast roll are recorded. The alkalinity of the sample was determined by the benzene-alcohol-water digestion method described by Palmer and Miller[3]. Tensile tests of the reclaims were obtained in test formulas I and II (Table II); these are the same as formulas IV and

TABLE II

TEST FORMULAS

| Formula No.<br>Type | I<br>Mechanical<br>molded goods | II<br>Tire<br>carcass | III<br>Tire<br>tread |
|---|---|---|---|
| Smoked sheet | 10.00 | 31.62 | 35.00 |
| Reclaimed rubber | 50.00 | 50.00 | 35.30 |
| Zinc oxide | 2.00 | 1.25 | 2.50 |
| Natural whiting | 15.30 | 12.00 | . . . |
| Clay | 20.00 | . . . | . . . |
| Channel black | . . . | . . . | 18.00 |
| Stearic acid | 1.00 | 0.75 | 2.00 |
| Pine tar | . . . | 2.00 | . . . |
| Mineral rubber | . . . | . . . | 5.00 |
| Sulfur | 1.40 | 2.00 | 1.80 |
| Diphenylguanidine | 0.10 | . . . | . . . |
| Mercaptobenzothiazole | . . . | 0.38 | 0.40 |
| Dibenzothiazyldimethylthiourea | 0.20 | . . . | . . . |
| | 100.00 | 100.00 | 100.00 |

III, respectively, proposed by Palmer and Crossley[4]. The reclaim-sulfur tensile tests were obtained by using the standard mix of 100 parts reclaimed rubber and 5 parts sulfur. Artificial aging was done by the air pressure heat test, as recommended by the American Society for Testing Materials[5].

The results of periodic chemical tests on reclaims A, B, and C are shown in Figure 1. In all cases the chloroform extract decreased as the reclaim aged, while the acetone extract remained fairly constant. The alkalinity of reclaims B and C remained constant but that of reclaim A tended to decrease somewhat irregularly. All reclaims became progressively drier, tougher, and nervier in processability with increased age, as shown in Figure 2. It is worthy of note that the milling properties of reclaim A, which has a high alkalinity, were least affected by age. This confirms previous observations in our laboratory that high alkalinity in reclaimed rubber tends to help preserve its original plasticity and workability during aging. The reclaim-sulfur tests shown in Figure 3 were somewhat inconsistent; no particular significance is attached to these results as the variability of this test is well known[6].

Tests of the reclaims in formula I as they increased in age are shown in Figure 4. For simplicity only one cure is plotted for each compound, but all cures in the range confirmed the trends noted. All reclaims tended to appreciate in normal tensile up to an age of 4 months and then to decrease. The
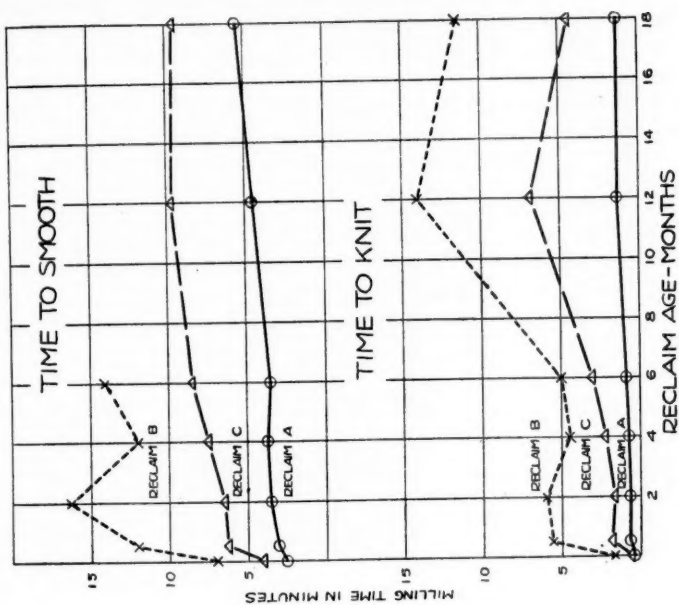
Fig. 2.—Effect of reclaim age on milling properties.
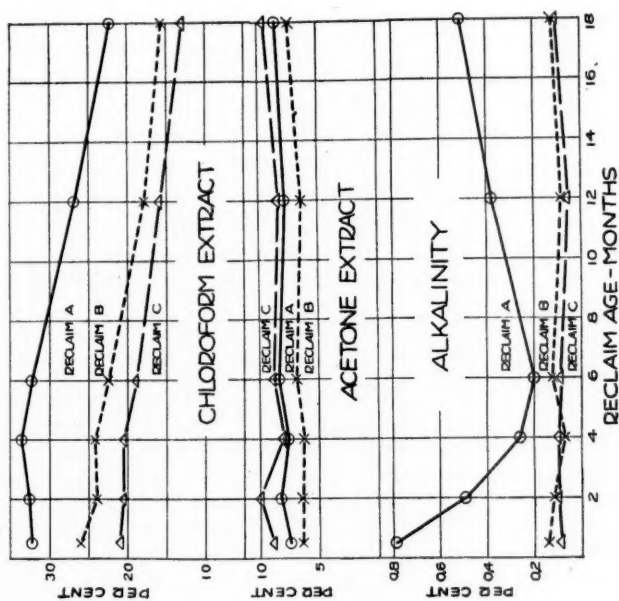


Fig. 1.—Effect of reclaim age on chemical properties.

tensile of reclaim A fell off uniformly after 4 months, aging after 18 months to a value only slightly lower than the 2-week test. Reclaim B behaved similarly, but its final tensile was somewhat lower than its 2-week value. The final tensile of reclaim C was superior to that obtained when it was 2 weeks old. Elongations appeared to be unaffected by the aging of the reclaims, and all reclaims seemed to improve with age in resistance to air bomb deterioration, although reclaim B was somewhat less consistent than the others.

Similar trends were observed in formula II, Figure 5. The normal tensile of all reclaims reached a maximum after 2 months, then decreased gradually up to an age of one year. After 18 months the tensile of reclaim A was somewhat lower than the 2-week value, while the tensiles of reclaims B and C rose
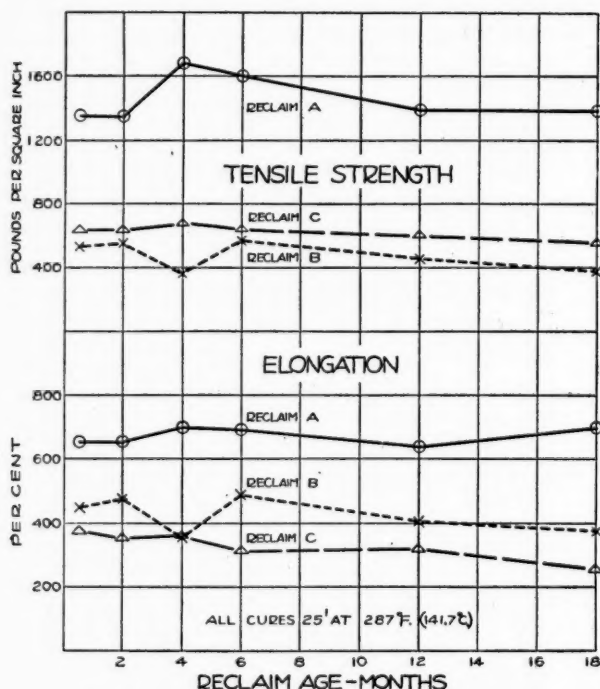


Fig. 3.—Effect of reclaim age on reclaim-sulfur tests.

to values equal to or higher than the 2-week values. As in formula I, elongations were not affected by the aging of the reclaims. Air-bomb tests on all three reclaims improved as the reclaims increased in age up to one year, but appeared to decrease somewhat after the reclaims had aged 18 months. Considerably more fluctuation from test to test was experienced with reclaims B and C than with A; it may be significant that the reclaims which behaved most erratically were of low alkalinity; the one giving the most consistent results was high in alkalinity. This behavior suggests that the alkalinity of a reclaim may have a beneficial effect on the age resistance of compounds in which it is used as well as on the preservation of the processability of the reclaim itself. In any event, there is no evidence in the above data that the samples of reclaimed rubber deteriorated in quality after 18 months of aging.
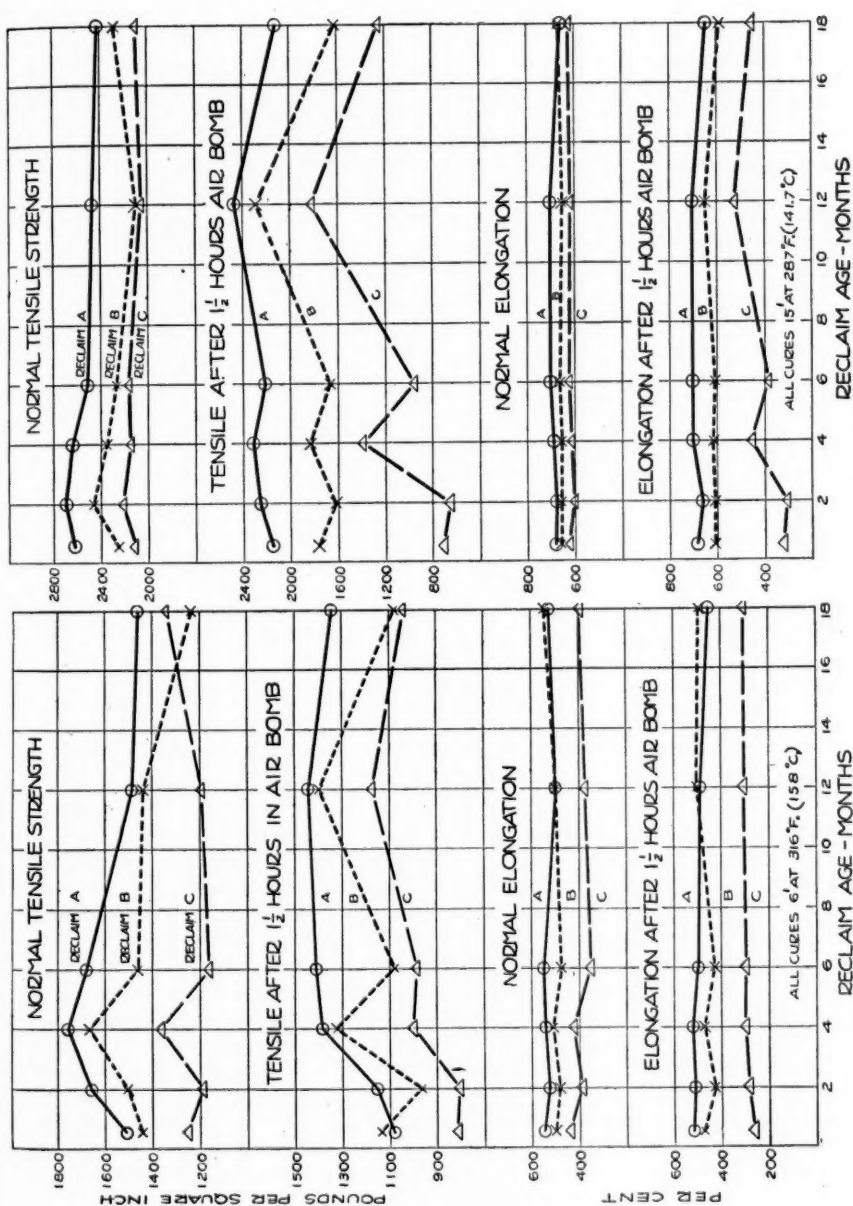
Fig. 5.—Effect of reclaim age on formula II.
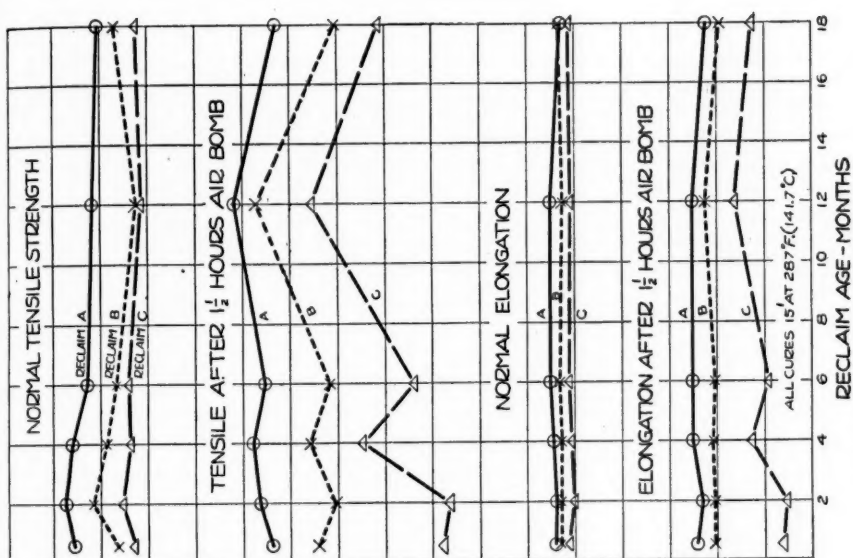
Fig. 4.—Effect of reclaim age on formula I.

## COMPARISON OF AGED AND FRESH RECLAIM

There are two ways in which this can be studied. First, a sample of reclaimed rubber may be set aside and tested at any desired interval as it ages, as was done in the experimental work described above. A second method is to manufacture lots of the reclaim at definite intervals and test them all simultaneously. It seemed desirable to use the second method to test the effect of natural aging of whole tire reclaim C on the quality of a tire tread compound, since this type of reclaim is widely used for the purpose. Accordingly, a pile of scrap tires large enough to make four separate lots of reclaim C was chosen, and four portions were reclaimed at definite intervals and tested together as described below. These lots were called C-1, C-2, C-3, and C-4, to indicate the order in which they were made. Their physical and chemical characteristics are shown in Table III. All are similar in processability, and

### TABLE III
#### CHARACTERISTICS OF RECLAIMS TESTED

| Reclaim No. Date made[a] | C-1 5-17-40 | C-2 11-8-40 | C-3 11-15-40 | C-4 5-16-41 |
|---|---|---|---|---|
| Analysis (percentages) | | | | |
| Acetone extract | 9.17 | 9.20 | 7.80 | 7.17 |
| Ash | 16.35 | 18.15 | 18.60 | 19.32 |
| Alkalinity | 0.11 | 0.12 | 0.10 | 0.08 |
| Specific gravity | 1.15 | 1.17 | 1.17 | 1.18 |
| Reclaim-sulfur test (25-min. cure at 287° F.) | | | | |
| Stress at 300% (lbs. per sq. in.) | 490 | 405 | 460 | 520 |
| Elongation (percentage) | 330 | 370 | 320 | 380 |
| Tensile (lbs. per sq. in.) | 570 | 525 | 505 | 690 |
| Milling test | | | | |
| Age (days) | 6 | 3 | 8 | 5 |
| Smooth time (min.) | 4.8 | 5.0 | 5.0 | 5.0 |
| Knit time (min.) | 1.0 | 1.3 | 1.6 | 0.8 |
| Fast roll time (min.) | 5.0+ | 5.0+ | 5.0+ | 5.0+ |

[a] Reclaims were approximately one week old when these tests were made.

the greatest variation in chemical tests occurs between lots C-1 and C-4. The variation in ash and specific gravity is not unusual for this reclaim, for dusting pigment is used during the manufacturing process, which unavoidably influences these properties. Physical tests were obtained in a typical third-line tire tread, formula III (Table II), from which the antioxidant was purposely omitted to bring out any differences in aging characteristics which might occur.

Reclaims C-1, C-2, and C-3 were made up at intervals so that, when tested in formula III, they were 6 months, 6 weeks, and 1 week old, respectively. The results are shown in Figure 6. Normal physical tests indicate very little difference beyond a slight stiffening on the part of C-1. Air-bomb aging tests[5] show C-1 to be slightly poorer, although not seriously so, while abrasion resistance as determined by the du Pont abrader[5] was equal for all three reclaims. Their resistance to heat build-up and blow-out or rupture during flexing was substantially the same as measured on the Firestone Flexometer. As described by Cooper[7], this test consists in compressing, under definite load, a block of rubber between two plates; one is stationary while the other travels in a circular motion of definite magnitude at constant speed. Temperature rise measurements are made by inserting a thermocouple in the block after a certain interval, and the time necessary to rupture the block is measured.
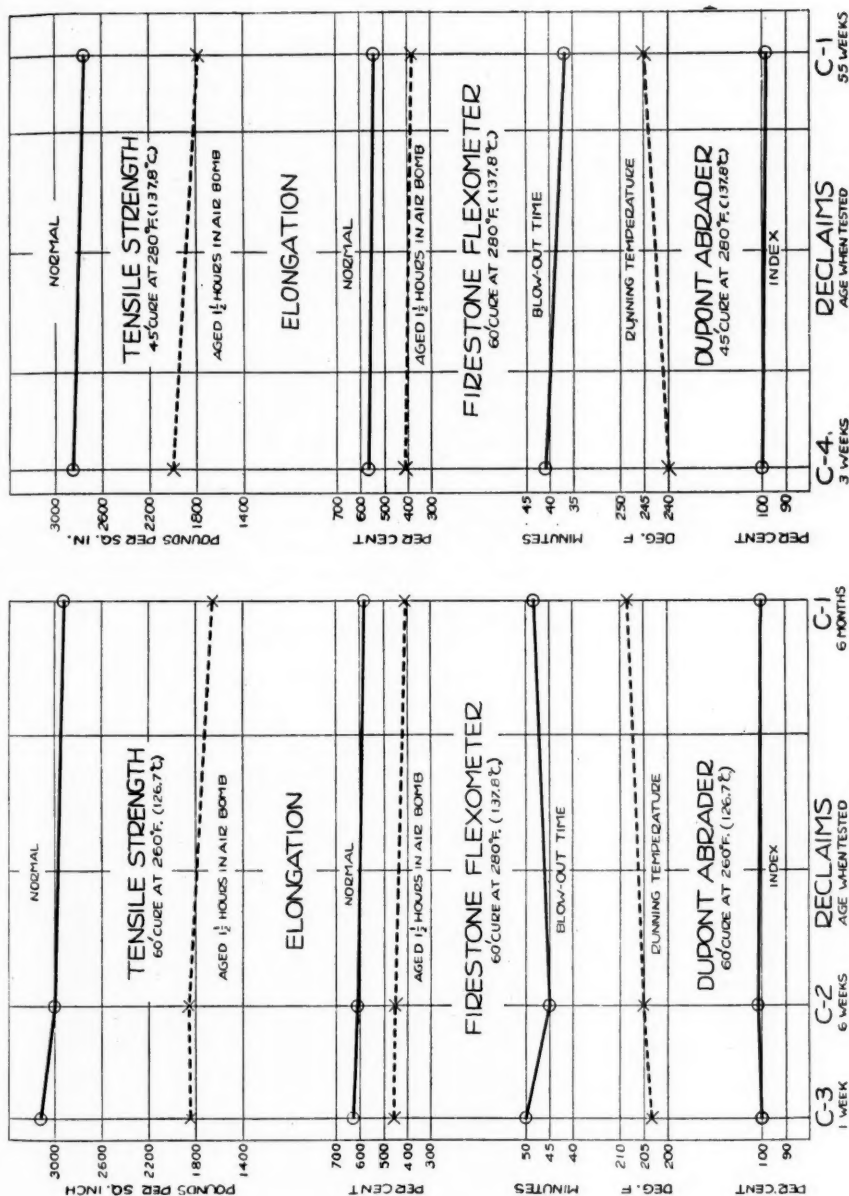
Fig. 7.—Reclaims in formula III.
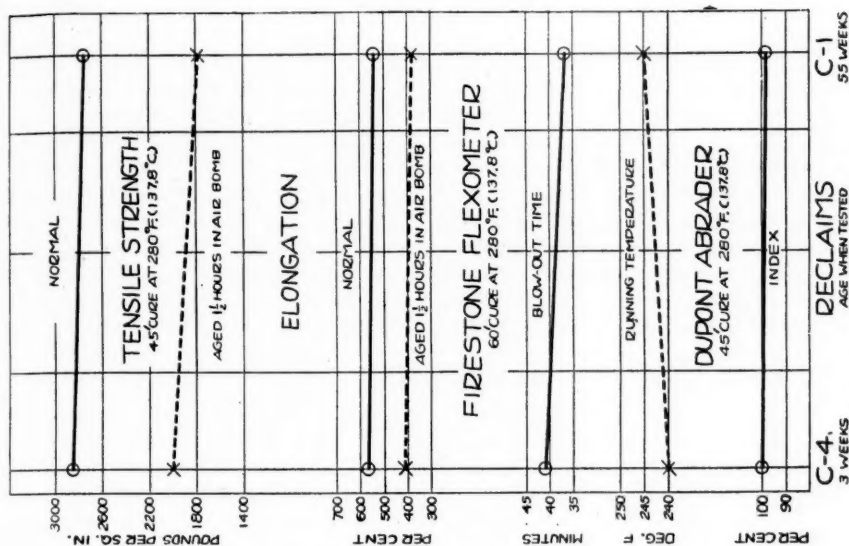
Fig. 6.—Reclaims in formula III.

After reclaim C-1 was one year old, reclaim C-4 was made up and both were again tested in formula III, with results as shown in Figure 7. Except for slightly poorer air-bomb aging tests, the one-year-old reclaim C-1 is equivalent to fresh reclaim C-4.

As a confirmatory test, reclaims C-1 and C-4 were compared in 22 per cent quantities in the treads of standard 6.00 × 16 tires under standard road test conditions. The reclaims were aged 3 and 15 months when the tires were built. The tires were run on test cars under identical conditions for approximately 10,000 miles; then they were removed and inspected for wear and cracking. The tires containing 15-month-old reclaim C-1 were slightly superior to those containing 3-month-old reclaim C-4 in resistance to tread cracking and were approximately 6 per cent poorer in wear resistance. It was felt that these differences were no greater than the normal variation to be expected between any two lots of this reclaim, and only slightly greater than the normal variation between any two sets of test tires.

## CONCLUSIONS

As reclaimed rubber undergoes natural aging, it becomes less tacky and more resistant to breakdown during milling. This appears to be true to a lesser degree for reclaims having a high alkalinity than for those with low alkalinity. The acetone extract of reclaimed rubber remains constant as it ages, but its chloroform extract tends to decrease. These changes are accompanied by only small variations in physical properties, as shown by results obtained in typical test formulas. There is no significant change in quality when reclaim up to 18 months of age is used. This was true also of tire treads containing reclaim aged 15 months, as judged by actual road tests.

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# SPONGE RUBBER *

## A. Cooper

It is the object of this paper to deal with some of the less known facts concerning sponge rubber, and not with latex sponge, frothed sponge[1] or sponges made by specialized processes, such as the Goodrich and Lindemann methods already described by Brazier[2], or sponges produced from rubber solutions and spraying processes, or other specialized methods recently developed.

In the manufacture of sponge rubber the greatest problem is the plasticity and uniformity of the raw rubber, and more attention has been given to this than to any other aspect of the manufacture of sponge; yet there is still ample room for development and improvement in this connection. Blending and batching of raw rubber and plasticity control are constantly advocated, and the importance of such standardization cannot be overemphasized. Cold breakdown and mastication, chemical plasticizing and the addition of various softeners, factices and reclaims all have their applications, and can be varied according to requirements.

The degree of breakdown of the crude rubber, the use of softeners in the compounded mix and the balance between the type of blowing agent, rates of blowing and curing are the all-important inseparable factors of sponge work.

To supplement the information already available, the relative effects of various blowing agents have been studied in greater detail. These have been divided into three groups, i.e., those which bring about a sponge formation by: (1) chemical decomposition or dissociation, e.g., sodium bicarbonate, ammonium carbonate, sponge paste, and diazoaminobenzene; (2) chemical reaction, e.g., stearic acid and whiting, oleic acid and zinc powder; and sodium nitrite and ammonium chloride; and (3) volatilization, e.g., alcohol or methylated spirit, water, benzene, xylene, toluene, paraffin oil and carbon tetrachloride.

The question is often asked as to the relative blowing powers of these agents. A simple comparative test to ascertain this was performed in a high-pressure vapor bomb. The apparatus is shown in Figure 1. It consists of a small bomb of about 20 cc. capacity, having a screw-on plunger lid and a high-pressure sealing washer. The vessel is connected by a short steel tube to a pressure gauge, and is immersed in a bath of glycerine, which can be heated gradually with periodical stirring. Ten g. of each blowing agent were in turn placed in the bomb. The plunger lid could be so adjusted by means of thick or thin washers that practically all air could be eliminated. The test in each case was commenced at room temperature, and gradually increased over a period of two hours to 170° C, which was considered the highest temperature which would be reached under practical conditions of vulcanization.

The pressure exerted at various temperatures was recorded in each case, and Figure 2 shows the behavior of the blowing agents or mixtures. These figures are only comparative.

*Sodium bicarbonate* is probably the most widely used blowing agent. From the graph it can be seen that sodium bicarbonate exerts a medium type of pressure compared with other blowing agents, which indicates that it is a blowing agent easy to control and safe in use.

*Ammonium carbonate* is also one of the oldest and well known blowing agents. It is more drastic in its effect than sodium bicarbonate. The graph indicates the comparatively high pressure obtained. Often this high pressure is a disadvantage, as the gases evolved may simply diffuse without raising the rubber. This is particularly true when large quantities of this blowing agent are used. Furthermore, as ammonium carbonate dissociates, its reformation on cooling may cause the collapse of the whole sponge. The best remedy in such a case is to break the skin by rolling the sheet in a mangle or between open rollers, whereupon the original mould size is regained.
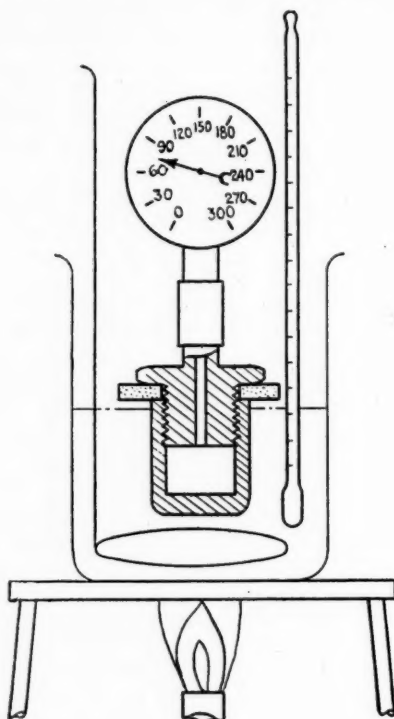


Fig. 1.

*Sponge paste* is a proprietary article. No information as to its exact composition is available except that it is a finely dispersed paste in an oil medium. There is reason to believe it contains a mixture of sodium bicarbonate and ammonium carbonate, and possibly some other ingredients. If this is so, it confirms the experience which many have had in mixing the two blowing agents to get a combination of their advantages, sodium bicarbonate for reliable steady blowing and ammonium carbonate for rapid blowing and the formation of sponge of lighter density.

*Diazoaminobenzene* produces fine cells and, therefore, has many advantages. Its decomposition to liberate nitrogen is a vigorous one, which accounts for only small percentages being necessary. Particular care should be exercised in handling this chemical, as it gives rise to dermatitis.

*Stearic acid and whiting* can be used quite effectively, although for good sponge formation extremely well masticated and softened rubber must be used, since the pressure produced is low, as will be seen from Figure 2.

*Oleic acid and zinc powder.*—The reaction between these substances produces cells which are fine, and resemble those produced by diazoaminobenzene.
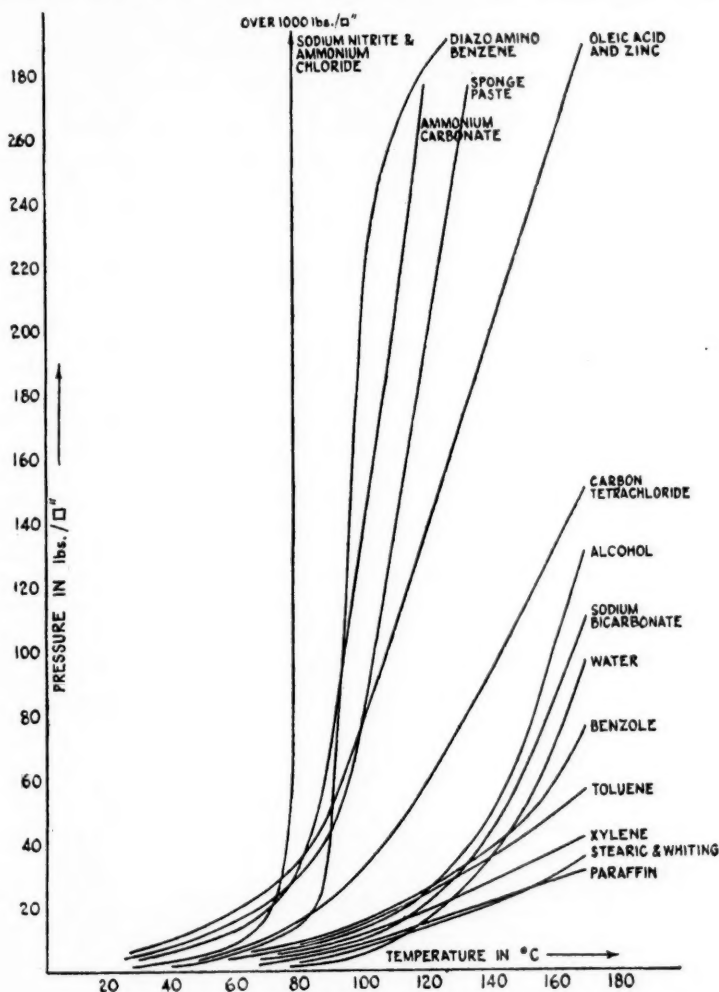


FIG. 2.

A fairly high pressure is generated, as can be seen from Figure 2. Its resemblance to diazoaminobenzene is evident, and it is noteworthy that these two blowing agents are the only ones with a vigorous blowing effect which produces small cells. Ammonium carbonate and the half-and-half mixture of sodium nitrite and ammonium chloride both give similar pressures, but large cells. There is a double advantage in using the oleic acid and zinc mixture, as the oleic acid serves also as a good softener and plasticizing agent.

*Sodium nitrite and ammonium chloride.*—It is doubtful whether the reaction between these chemicals shows any particular advantages, since the reaction is almost explosive in character at a temperature as low as 79° C; hence nitrogen would be evolved before the rubber became plastic.

*Volatile blowing agents* include water and alcohol, which are mixed into the batch in a paste form with either zinc oxide or fillers. The other volatile agents have the advantage of dissolving the rubber or dissolving into the rubber and, therefore, act also as softeners. Light-density sponges are invariably made by these methods. The most important thing in connection with the use of volatile blowing agents is the choice of accelerators. Whereas normally accelerators for sponge rubber should have sufficient curing-lag or delayed action to allow blowing to take place before vulcanization, when using volatile blowing agents faster accelerators should be used to give a semi-vulcanization before the blowing commences; otherwise the vapors simply diffuse out of the mix.

It is often found convenient to select a chemical blowing agent and a volatile type and use them together. The effect is a sponge with both large and small pores which has softness and strength combined. Furthermore, combinations of various blowing agents often give good results. Stearic acid or oleic acid, for example, when used in conjunction with sodium bicarbonate will increase the blowing action, giving products of lighter density.

The foregoing results with reference to Figure 2 may be regarded as only of general interest and as having little practical application, but when going more fully into the matter it will be noted that most sponge troubles are influenced by the blowing power of the sponging agent. Apparent density, compressibility, size of pores, absence of surface depressions and pits, local air pockets and many other factors are affected wholly or partly by the blowing agent. The results also may have a bearing on the process and mould design.

A further series of tests was made to ascertain the pressure exerted by different quantities of various blowing agents when incorporated into a rubber mixture. The apparatus for this is shown in Figure 3. It consists of a mould
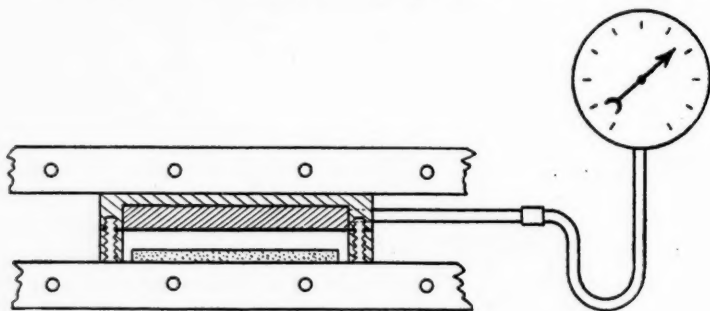


FIG. 3.

divided into two parts by a thin spring steel diaphragm. The lower part is used for the vulcanization of the sample and the upper chamber or compartment is filled with mercury and is connected with a mercury-filled steel tube to a pressure gauge. The curing time and temperature were constant for all mixes, *viz.*, 50 minutes at 150° C, and the highest pressure obtained for each test was recorded in Figure 4.

The curves correspond more or less with those obtained in the vapor bomb experiment. The mixes used are shown in Table 1, but should not be regarded as necessarily the best of their kind, for each blowing agent as a number of factors such as aging, etc., have not been taken into account. The mixtures were merely selected for the purpose of giving comparative figures.
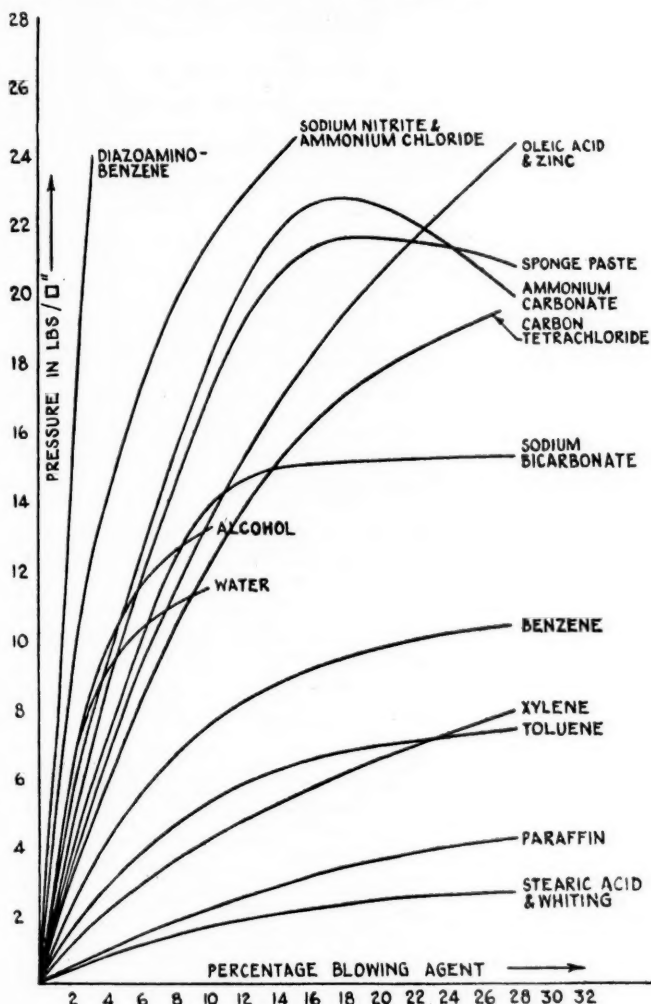


FIG. 4

The smallest and largest recommended proportions of blowing agents were used, so that in each case a series of mixes was made, as indicated in the table. In the case of the volatile blowing agents, it was necessary to use a faster accelerator, as already indicated. In some cases it will be noted that, even if high percentages of blowing agents were used, the resultant pressure was no greater, and in some cases even less. This is attributed to the fact that a

<div align="center">TABLE 1</div>

| Base Mix. | Pale crepe rubber | 100 |
|---|---|---|
| | Plastaid | 5 |
| | Vaseline | 15 |
| | Stearic acid | 3 |
| | Zinc oxide | 3 |
| | Sulfur | 2 |
| | Accelerator | 1 |

With the following blowing agents, benzthiazyl disulfide was used as accelerator:

| Sodium bicarbonate | 5 to 30 | Sodium nitrite and ammonium chloride | 5 to 20 |
|---|---|---|---|
| Ammonium carbonate | 5 to 20 | | |
| Sponge paste | 5 to 20 | Stearic acid and whiting | 5 to 15 |
| Diazoaminobenzene | 1 to 5 | Alcohol | 2 to 6 |
| Oleic acid and zinc powder | 5 to 15 | Water | 2 to 6 |

With the following blowing agents, Vulcacit F. was used as accelerator:

| Benzene | 5 to 15 | Paraffin oil | 5 to 15 |
|---|---|---|---|
| Toluene | 5 to 15 | Carbon tetrachloride. | 5 to 15 |
| Xylene | 5 to 15 | | |

The densities of the resulting sponges are plotted against the weights of blowing agent per 100 of rubber in Figure 4.

certain amount of diffusion takes place with excess blowing agent. This fact is also borne out in the later experiments on the same mixtures, where the effect of varying quantities of blowing agents on the apparent density of the finished sponge is investigated.

The softness of a sponge depends largely on its apparent density, which in turn depends on the type and quantity of softener, blowing agent, accelerator
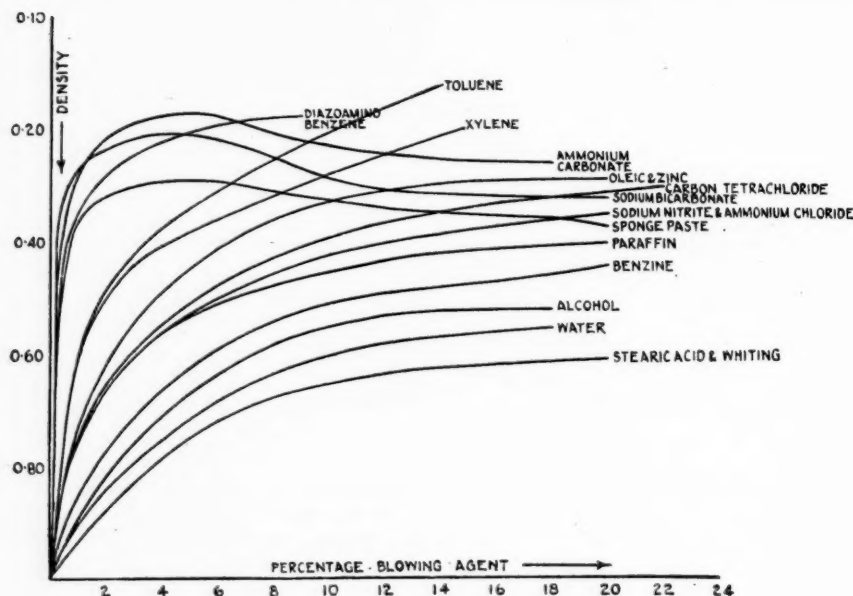


FIG. 5.

and fillers. The type of softener is not exactly a critical matter, provided enough is present to render the batch sufficiently plastic. It is easy to use excess softeners, and then find that the gas or vapor produced from the sponging agent simply diffuses out of the mixture at the commencement of vulcanization, instead of raising the rubber. In other words, the same effect takes place as with excess blowing agent.

Figure 5 shows the effect of an increased amount of blowing agent on the apparent density. At the same time Figure 5 shows an approximate comparison between the suitability of various blowing agents for producing materials of light density. The diffusion with excess quantities of blowing agents can be arrested by using greater percentages of accelerators. This remedy is often erroneously applied.

From the production aspect, the satisfactory curing of sponge rubber often presents difficulties, but if a few simple principles are observed these should be overcome. All moulds or curing frames should be properly vented to prevent trapped air in the mould and the tendency for the formation of gas pockets as the sponge rises and completely fills the mould. As the sponge rubber increases in volume it has to displace its own or twice its own volume of air, as the case may be. The formation of an air cushion which hinders the free increase in volume can be avoided by a further precaution (which is particularly applicable in the case of sponge rubber sheeting) of placing the curing frame between well-chalked heavy duck. The trapped air is thereby allowed to escape through the fibres of the cloth. Asbestos cloth or sheeting can often be used with advantage to prevent surface or local overheating[3].

These experimental results may assist in putting the vast amount of theoretical knowledge of sponge production into practice, particularly when dealing with the problem of striking a correct balance between plasticity, blowing agent and accelerator, which not so long ago seemed reached by trial and error methods.

In conclusion, the writer wishes to express his thanks to the Chairman and Managing Director of Expanded Rubber Company for their kind permission to read this paper.

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# PRODUCTION OF INDUSTRIAL
# SPONGE RUBBER *

## E. J. MAY

The production of sponge rubber for industrial use not only involves the blowing of a mass of plastic rubber compound to a given shape of predetermined density, with concurrent vulcanization, but also the production of a sponge product which will withstand the same severe conditions as will solid rubber produced by modern compounding.

Until recent years, the aging and heat-resisting properties of sponge rubber left much to be desired, mainly because of the large surface area susceptible to oxidation, and the large amounts of oils and softeners used to plasticize the rubber. The oils themselves, far from beneficial to aging properties, necessitated in many cases high sulfur ratios to restore the nerve to the vulcanized sponge. It is, however, necessary to plasticize the raw rubber to obtain satisfactory blowing. Within limits, the pore size and density of a sponge from a given stock are governed to a greater extent by the plasticity of the mixed compound than by the amount of blowing agent contained in the stock. To obtain maximum physical properties, the method of plasticizing which has the least deleterious effects on the vulcanized product has to be chosen. This may be one, or a combination of, the following: (1) breakdown of the crude rubber on cool mixing rolls; (2) hot breakdown of the crude rubber at temperatures above 120° C on open rolls or in an enclosed mixer; (3) use of chemical plasticizers; (4) use of plantation softened rubber, such as that produced by the Socfin Co. of Malaya, or by the Schidrowitz-Ungar process, and (5) addition of large quantities of softening oils during mixing.

The raw rubber usually found most satisfactory is pale crepe, since it requires less breaking down than smoked sheet, and is not so variable as brown crepes. Of the methods of plasticizing, (1) appears to give the best results, although all are satisfactory with the exception of (5).

*Compounding.*—The compounds used are generally those which do not stiffen the unvulcanized stock. Whiting, barytes and lithopone are the usual fillers, although, where medium density sponge is desired, substantial quantities of soft blacks can be used with surprisingly good results.

Accelerators play an important part in the production of industrial sponge. The accelerators or accelerator combinations which can be used with either low sulfur or sulfurless compounding, and at the same time have a delayed action, are the most advantageous. Sponge sealing strips can be produced, using 3 per cent to 5 per cent of tetramethylthiuram disulfide on the rubber content and no sulfur, or as a cheaper combination, 0.5–1 per cent of sulfur in conjunction with smaller quantities of tetramethylthiuram disulfide and benzothiazyl disulfide may be used. It is important that the curing media should give a flat cure, as it is necessary to be certain that the sponge is well cured throughout, without unduly overcuring the surface.

Blowing agents may be any of the usual combinations, but the effect on cure and aging properties should be carefully studied. Antioxidants should be in the region of 2 per cent, based on the rubber content of the stock.

Sponge articles produced from stocks developed on these lines have far greater resistance to aging and heat deterioration than normal sponge compounds. As shown later, vulcanizates that show no signs of deterioration after 100 hours at 120° C, and are apparently unaffected after 21 days' oxygen-bomb aging (300 lbs. per sq. in. oxygen at 70° C), have been produced. Stocks loaded with soft black and using "sulfurless" cure also have far superior resistance to oil, although they cannot be termed oil-resisting, owing to the fact that swelling is encountered when in contact with oil. Compounds of this type under test, however, showed no surface solution, and were still in a strong condition, after immersion in oil for 24 hours at 120° C, although a dimensional increase of 15 per cent was encountered; whereas standard commercial sponge samples of similar density, tested at the same time, completely disintegrated under test. It is, therefore, indicated that where service conditions do not involve contact with oil sufficient to merit the use of synthetic sponge or protective synthetic skin, but merely oil splashes, this type of rubber sponge compound would prove satisfactory.

Certain industries call for sponge rubber which will not tarnish copper or silver surfaces when in contact with them. For this purpose, low sulfur or sulfurless compounding is of great value, as a free sulfur figure of below 0.01 per cent is called for by the users of this material.

Neoprene sponge can be quite easily produced, especially with Neoprene-GN, which can be plasticized with diorthotolylguanidine and stearic acid, as well as with the usual factices, oils and softeners. An added advantage is that cure is not retarded by stearic acid to any great extent, as with the older types of Neoprene, thus enabling sodium bicarbonate and the fatty acid to be used as a blowing medium. Neoprene sponge is more oil-resisting than rubber vulcanizates, but unless care is taken, the heat-resisting properties of Neoprene sponge may be impaired by factice and oils used as plasticizers.

Where flame-resisting sponge is required, Neoprene is of value. Sponge which will not continue to burn after the removal of an applied flame can be produced using a Neoprene stock in which inflammable oils and waxes have been replaced by noninflammable chlorinated hydrocarbons, and such softeners as tricresyl phosphate.

Simple rubber sponge mouldings, such as sealing strips, can be protected against oil by vulcanizing on a thin Neoprene skin in the region of 1/64 inch thick; irregular shapes, however, are more difficult to protect in this manner. The degree of protection depends on the resistance of the thin Neoprene skin to the oil. Surprisingly good results are obtained, providing the skin affords a complete seal over the natural rubber sponge.

An aspect of sponge rubber production which has developed in importance considerably within the past year is resistance to cold. A sponge rubber antivibration or sealing strip is of little use on aircraft at high altitudes if it becomes hard and brittle at the low temperatures encountered. There is little available information on this subject, but initial experiments have shown that undercure should be avoided, and that plasticizing oils should be of the nonfreezing types. Sponge rubber sealing strips that retain their ability to recover after compression at temperatures down to −40° C have been produced. With further lowering of the temperatures, however, they progressively stiffen until, at −65° C, the samples become brittle and snap on bending. In this connection, it is interesting to note that a new type of Neoprene designed to be cold-resisting is available in the United States.

For aircraft work where sponge rubber comes into contact with light metal alloys, it is specified that the aqueous extract from the sponge shall be almost neutral, and the $p$H value of the extract must be between 6 and 8.   Even with solid rubbers the compound must be carefully adjusted to achieve this, and with sponge it is most difficult to obtain a product which gives an extract with a $p$H value between the specified limits.   However, much may be done by a careful choice of blowing agents and adjustment of the mixture to avoid as far as possible alkaline residues after vulcanization.

Sponge rubber can be quite satisfactorily bonded to metal by the brass-plating method.   It is necessary, however, to use a normal sulfur compound. A rubber-to-metal bond which is stronger than the sponge itself can be obtained.

## APPENDIX

### DETAILS OF COMPOUNDS AND RESULTS OF TESTS CARRIED OUT

The composition of the sponges used in the test are given in Table 1.

#### TABLE 1

|                                   | A     | B    | C   | D   |
|-----------------------------------|-------|------|-----|-----|
| Pale crepe rubber                 | 100   | 100  | 100 | 100 |
| Whiting                           | . . . | 30   | . . . | . . . |
| P-33 soft carbon                  | 50    | . . . | . . . | 50  |
| Petrolatum                        | . . . | 10   | . . . | . . . |
| Plastogen oil                     | 10    | . . . | . . . | . . . |
| D.T.D. 44.B. oil                  | . . . | . . . | 10  | 10  |
| Stearic acid                      | 5     | 10   | 5   | 5   |
| Sodium bicarbonate                | 5     | 10   | 5   | 5   |
| Nonox-S                           | 2     | 1.5  | 2   | 2   |
| Zinc oxide                        | 5     | 5    | 5   | 5   |
| Sulfur                            | 1     | . . . | . . . | . . . |
| Tetramethylthiuram disulfide      | 0.375 | 5    | 5   | 5   |
| Benzothiazyl disulfide            | 0.5   | . . . | . . . | . . . |

| *Neoprene sponge*        | E    |
|--------------------------|------|
| Neoprene-GN              | 100  |
| Stearic acid             | 1    |
| Diorthotolylguanidine    | 0.5  |
| Brown substitute         | 30   |
| Mineral oil              | 20   |
| P-33 soft carbon         | 5    |
| Nonox-S                  | 2    |
| Zinc oxide               | 2    |
| Light magnesium oxide    | 4    |
| Sodium bicarbonate       | 10   |
| Stearic acid             | 10   |

Samples were press-cured, in strip moulds for 20 minutes at 150° C, to a density of 0.35.   Commercial samples tested were of similar density; and contained 3 to 4 per cent sulfur and 1.5 per cent of antioxidant, based on the rubber content.

All samples tested, except the Neoprene-covered samples, were moulded strips of similar length with a natural skin, except at the ends, where they had been cut and the open sponge texture was exposed.   Neoprene-covered samples had a solid Neoprene skin approximately 1/64 inch thick, and no open ends were exposed.

During the aging tests, the samples were compressed daily to expel any stale air or oxygen in the cells.

**TABLE 2**

| Test | | Commercial samples | | | Low sulfur | Sulfurless sponges | | | Neoprene |
|---|---|---|---|---|---|---|---|---|---|
| | | (1) | (2) | (3) | A | B | C | D | E |
| Immersion in D.T.D. 109 oil at 120° C. | 24 hrs. | Surface solution. 12% increase in length. Penetration not complete | Disintegrated | Completely disintegrated | Still strong. 38% increase in length. Complete penetration | Still strong. 25% increase in length. Complete penetration | Still strong. 15% increase in length. Penetration not complete | Still strong. 10 to 12% increase in length. Penetration not complete | Still strong. 5% increase in length. Complete penetration |
| Hot air oven test at 120° C. | 24 hrs. | Exceedingly short. Would not stand doubling over | Exceedingly short. Would not stand doubling over | Complete breakdown | Still in excellent condition (A, B, C, D) | | | | > |
| | 48 hrs. | Not continued after 24 hours | | | Still in good condition (A, B, C, D) | | | | Became short, but did not crack on bending |
| | 96 hrs. | All showed signs of perishing except D. Order of merit—D, C, A, B | | | | | | | > |
| Oxygen-bomb. Test at 70° C. and 300 lbs. per sq. in. oxygen pressure | 90 hrs. | No apparent change | No apparent change | Surface disintegration commenced. Withstands 100% elongation | No apparent change (A, B, C, D) | | | | > |
| | 200 hrs. | Considerable surface disintegration. Withstands 100% E | Surface disintegration commenced. Withstands 100% elongation | Completely disintegrated | Disintegrated | No apparent change (B, C, D) | | | > |
| | 330 hrs. | Disintegrated | Disintegrated | | | No apparent change (B, C, D) | | | |
| | 500 hrs. | | | | | No apparent change. All samples withstood 100% elongation without cracking, and no permanent set on release (B, C, D) | | | Surface apparently unaffected; would not withstand 100% E |

TABLE 2—Continued

| Test | | Commercial samples | | | Low sulfur | Sulfurless sponges | | | Neoprene |
|---|---|---|---|---|---|---|---|---|---|
| | | (1) | (2) | (3) | A | B | C | D | E |
| Resistance to low temperatures | | Loss of resilience commenced at −40° C. Brittle at −65° C | — | — | — | — | Loss of resilience commenced at −40° C. Brittle at −65° C | Loss of resilience commenced at −40° C. Brittle at −65° C | Loss of resilience commenced at −30° C to −35° C. Brittle at −55° C |
| Tarnishing of silver surfaces | | <———— | All tarnish ————> | | Did not tarnish | <———— | Did not tarnish | < > | Tarnishes |
| Air bomb. Test at 80 lbs. per sq. in. air pressure and 127° C | 3 hrs. | Would not stand 100% E. Loss of resilience | Became exceedingly short. Complete loss of resilience | Disintegrated | Withstood 100% E, but showed surface cracking | <———— | No apparent change ————> | ————> | Would not stand 100% elongation |
| | 20 hrs. | Not continued after 3 hrs. | | | Lost resilience and softened. Surface cracked | Withstood 100% E. Slight loss of resilience | No apparent change | No apparent change | Became exceedingly short and brittle |
| | 44 hrs. | | | | | Would not stand 100 % E. Loss of resilience | Became short, slight loss of resilience | Withstood 100% E. Slight loss of resilience | |

The silver tarnishing test was carried out in a hot air oven at 120° C. The samples were clamped to a silver surface for 30 minutes, after which the effect was noted.

The results of the test are given in Table 2.

It should be pointed out that the Neoprene sponge was not specially compounded to be heat- or cold-resisting, but was considered to be representative of a standard Neoprene sponge stock. The staining on silver by the Neoprene sponge was probably due to free sulfur in the brown substitute.

Sponges A and B with Neoprene skins were tested for resistance to immersion in D.T.D. 109 oil, and it was found that there was neither penetration nor change in dimensions.

### ACKNOWLEDGMENT

# ACCELERATORS AND COLORS
# IN SPONGE RUBBER *

## John T. Watts

The class of products falling under the generic name of sponge rubber may be subdivided into two main sections, depending solely on whether the pores are closed or open.

Closed pore structures, in which the gas cells retain their individuality, are characterized by cell size and hardness of the vulcanizate. This latter may vary from the softness of toilet-sponge to the hardness of ebonite. Among the softer grades of closed pore sponge, some of the contributing factors to softness of texture are: (1) the method and degree of plasticizing the raw rubber, (2) the ratio between raw rubber, fillers and softeners, and (3) the type of accelerator used.

Open-pore structures include latex sponge and cellular rubber in which the gas cells have been ruptured by mechanical means after curing. For the purpose of this paper the position is simplified by considering latex sponge alone as an open-pore sponge, as the mechanical operation for the production of open-pore from closed-pore sponge follows the rubber manufacturing process.

The closed-pore structure in rubber is usually produced by compounding with gas- or vapor-producing materials which, with change in temperature during cure, either liberate gas or change in phase to produce individual cells in the rubber compound. Alternatively, gas (usually nitrogen or carbon dioxide) may be dissolved in the rubber compound under pressure and the stock inflated by either rise in temperature or decrease in pressure, or both.

Uniform inflation can be obtained only in a stock which is more plastic than usually associated with rubber gum stocks. For this reason, the first essential is that there shall be no preliminary stiffening or skin effect due to set-up before cure, due either to the accelerator or to the combination of accelerator and blowing agent. Any peptizing action resulting from the use of a particular accelerator is an added advantage.

In the initial stages of the vulcanizing period, the rubber stock is transformed into a fluid state and inflation begins. Good inflation results in a series of gas bubbles, fairly uniform in size, filling the mould. During this period the accelerator should remain inactive and allow the fluidity of the mass to give the blowing agent its full effect. After inflation, however, vulcanization should immediately impart rigidity to the extended cell walls, i.e., the temperature of activation of the accelerator should be fairly close to the final temperature of the inflation period. Too early set-up during the blowing period results in a sponge which is incompletely blown, or in which the cell walls are thick in comparison to the cell size. Delay in vulcanization results in the collapse of small cells, and the product is devoid of thin cell walls, is irregular in structure, and has a thick rind. Where inflation and vulcanization are carried out at different temperatures, the inflating period is usually given as a preliminary rise, followed immediately by change to vulcanizing conditions.

On the other hand, inflation and vulcanization are quite frequently carried

out at the same temperature. In these circumstances the accelerator allows blowing to take place before the stock has set up, followed immediately by set-up and subsequent vulcanization. This is accomplished by the lag in temperature between the stock and platens, which is sufficiently great to enable this cycle of changes to take place.

*Characteristics of an ideal accelerator.*—The characteristics of an ideal accelerator for sponge rubber may be stated as follows: (1) plasticizing action on rubber stock, (2) absence of set-up during processing and storage, (3) absence of set-up during the period of inflation before vulcanization, (4) rapid set up and vulcanization at the final temperature of the inflation period, (5) good aging properties of vulcanizate, (6) nonstaining, (7) should work equally well with all blowing agents.

The Effect of Accelerator on Properties of Sponge Rubber.— A consideration of the entire speed range of accelerators shows that no one individual fits all the requirements of an ideal accelerator. Nevertheless, excellent sponge is made with a wide variety of accelerators, depending entirely on the requirements for service or sales in the finished product.

Very slow accelerators include condensation products of aldehydeamines, *e.g.*, formaldehydeaniline or formaldehyde-*p*-toluidine. In sponge rubber these accelerators require a long period of vulcanization after blowing is completed, and give products with only moderate aging qualities, and which are stained during vulcanization. Similar criticisms can be levelled at slow accelerators, such as thiocarbanilide.

Ultra-accelerators, such as xanthates and dithiocarbamates, are too fast in cure to be of much use in the manufacture of press-cured sponge, and find their major application in latex sponge.

The remaining classes, that is, medium, semi-ultra and delayed-action accelerators cover almost entirely all accelerators used commercially.

Medium accelerators represented by diphenylguanidine, di-*o*-tolylguanidine give satisfactory results under some conditions of cure (fairly long vulcanization periods for thick sponge), but have the disadvantage of staining whites or colors.

Semi-ultra accelerators, including butyraldehydeaniline, mercaptobenzothiazole and ethylideneaniline condensation product all give exceptionally good sponge. The aniline-condensation derivatives do, however, stain whites and colors.

Delayed-action accelerators, as their name implies, are inactive up to temperatures beyond the normal processing range, and then beyond their temperature of activation give snappy vulcanizates. An example is dibenzothiazyl disulfide.

The choice of accelerator therefore is restricted to a delayed-action type, mercaptobenzothiazole, or if discoloration is of no importance, a limited choice is available among the basic accelerators. The final decision can only be made with a complete knowledge of the cycle of manufacturing operations and the requirements of texture and nerve of the finished sponge.

A study of the scorching caused by various accelerators at 100° C does not entirely show the suitability of an accelerator for sponge rubber, as many of the blowing agents have an activating effect on the accelerator, which may be followed by noting the time taken for stock containing both to set-up in comparison to stock containing accelerators only.

The Influence of Blowing Agents on the Rate of Scorching of Accelerators.—The following mixture was prepared: pale crepe rubber, 100;

WITH SODIUM BICARBONATE AS BLOWING AGENT

| Type of accelerator | Texture and pore size | Discoloration |
|---|---|---|
| Slow aldehydeamines | Large-medium pores, lacking resilience | Stained |
| Condensation products of form-aldehydeaniline, etc. | Thick cell walls and heavy rind | Stained |
| Butyraldehydeaniline condensation product | Harsh-texture, medium pores, resilient | Stained |
| Diphenylguanidine and di-o-tolylguanidine | Harsh-texture, large-medium pores, heavy rind, lacking resilience | Stained |
| Ethylideneaniline condensation product | Soft texture, large-medium pores, fairly resilient | Stained |
| Mercaptobenzothiazole | Crisp texture, fine pores, re-silient | Not-stained |
| Dibenzothiazyl disulfide | Crisp texture, fine pores, re-silient | Not-stained |
| Tetramethylthiuram monosulfide | Crisp texture, fine pores, re-silient | Not-stained |

zinc oxide, 10; stearic acid, 1; whiting, 75; sulfur, 2.5; liquid paraffin, 5; blowing agent, 5; accelerator, 0.5.

The liquid paraffin and blowing agent were ball-milled together to ensure even distribution of the latter, except in the case of the rubber-soluble blowing agent, diazoaminobenzene.

MINUTES AT 100° C BEFORE SCORCHING OCCURS

| Accelerator | Control | Sodium bicarbon-ate | Ammonium bicarbon-ate | Diazo-amino-benzene |
|---|---|---|---|---|
| Mercaptobenzothiazole | 150* | 150 | 30 | 120 |
| Diphenylguanidine | 210* | 210 | 150 | ... |
| Butyraldehydeaniline | 80 | 70 | 30 | 70 |
| Tetramethylthiuram disulfide | 70 | 60 | 30 | 45 |
| Tetramethylthiuram monosulfide | 90 | 80 | 30 | ... |
| Ethylideneaniline type (Vulcafor-RN) | 210* | 210 | 60 | 120 |
| Ethylideneaniline type (Vulcafor-PT) | 210* | 210 | 150 | ... |

* Beginning to scorch, but to a smaller degree than when blowing agent is present.

The rate of scorching of mixes containing ammonium bicarbonate is outstanding in comparison to the other blowing agents tested.

To produce conditions closer to those holding in practice, a method of testing accelerators in sponge mixtures was developed some years ago in the Rubber Service Laboratories of Imperial Chemical Industries, Ltd., by noting the degree of inflation permitted before cure.

Various accelerators to be tested are compounded into a standard sponge mixture in equivalent proportions. Equal weights (10 g.) of the completed mixture are then placed at the end of a multicavity mould (9 × 1 × 0.5 in.), and cured in a press at temperatures ranging from 125° to 141° C (20 to 40 lbs. per sq. in. steam pressure). An average result from three different mixtures of the accelerator is taken as representing the extent of inflation under the conditions prevailing. The degree of inflation in a comparative set of experiments depends on the temperature of cure, the rate of cure of the accelerator, and the effect of blowing agent on the accelerator.

From the scorching times quoted, it is seen that the safety factor for processing of all these accelerators is such as to permit a fairly good degree of inflation.

The degree of inflation obtained under similar experimental conditions is given below. The slow aldehydeamine and the delayed-action type of accelerator show the largest degree of inflation, and indicate the general suitability of delayed-action accelerators in sponge manufacture, for, although a similar degree of inflation is obtained with aldehydeamines, the vulcanizate is badly discolored by the accelerator.

CURED AT 40 LBS. PER SQ. IN. STEAM PRESSURE (141° C)
*Blowing agent—sodium bicarbonate*

| Accelerator | Inflation (per cent) |
|---|---|
| *24 hours after mixing* | |
| Butyraldehydeaniline condensation product | 450 |
| Diphenylguanidine | 475 |
| Mercaptobenzothiazole | 475 |
| Dibenzothiazyl disulfide | 630 |
| Ethylideneaniline condensation product | 680 |
| *1 week after mixing* | |
| Butyraldehydeaniline condensation product | 350 |
| Mercaptobenzothiazole | 350 |
| Ethylideneaniline condensation product | 500 |

CURED AT 20 LBS. PER SQ. IN. STEAM PRESSURE (125° C)

| | |
|---|---|
| Mercaptobenzothiazole | 650 |

CURED AT 40 LBS. PER SQ. IN. STEAM PRESSURE (141° C)
*Blowing agent—ammonium bicarbonate*

| Accelerator | Inflation (per cent) |
|---|---|
| *24 hours after mixing* | |
| Diphenylguanidine | 675 |
| Mercaptobenzothiazole | 600 |
| Butyraldehydeaniline condensation product | 575 |
| Dibenzothiazyl disulfide | 650 |
| Ethylideneaniline condensation product | 675 |

The inflation figures with ammonium bicarbonate are in much closer agreement, and depend less on the type of accelerator used than in the case of sodium bicarbonate.

Thus far, consideration has been given to popular types of blowing agents and their effect on accelerators.

With the introduction of diazoaminobenzene, a blowing agent is available which produces a fine even cell structure, different from that obtained by sodium or ammonium bicarbonate. Owing to the solubility of diazoaminobenzene in rubber, inflation is remarkably uniform. The fineness of texture obtained with diazoaminobenzene varies slightly with the type of accelerator used and also the relative amounts of blowing agent and accelerator. With the delayed-action or slow accelerator, the pore size is larger than that obtained with semi-ultra accelerators.

The permanent set (percentage) was the set registered with samples of 10–10.5 mm. compressed to 6.2–6.3 mm. for 16 hours, and allowed to recover 4 hours before measurement of recovery.

The low percentage of inflation produced by diazoaminobenzene is due to the rapid set-up of the mixture during the blowing period, owing to the fact that diazoaminobenzene is itself a vulcanizing agent for rubber.

*Aging of sponge rubber.*—The aging of sponge rubber depends on the type of accelerator used, the order of aging being similar to that pertaining for rubber, but considerably shorter, owing to the large surface-area involved,

#### With Diazoaminobenzene as Blowing Agent

| Accelerator | Texture and pore size | Remarks |
|---|---|---|
| Condensation products of aldehydeamine, e.g., formaldehydeaniline, etc. | Soft texture, large-medium pores, tendency to be loggy | Increase in blowing agent to 5 parts per 100 rubber has little effect |
| Butyraldehydeaniline condensation product | Medium pores, tendency to be loggy | Slow in curing |
| Diphenylguanidine | Medium pores, tendency to be loggy | Slow in curing, increase in blowing agent improves slightly |
| Mercaptobenzothiazole | Fine pores | Pore size reduced and nerve increased by slight increase in blowing agent |
| Dibenzothiazyl disulfide | Fine—medium pores | Pore size reduced and nerve increased by slight increase in blowing agent |
| Mercaptobenzothiazole with tetramethylthiuram disulfide | Fine pores | Quicker cure than mercaptobenzothiazole alone |

| Accelerator | Accelerator Parts per 100 rubber | Diazoaminobenzene | Cure at 141° C | Inflation (percentage) | Permanent set (percentage) |
|---|---|---|---|---|---|
| Diphenylguanidine | 1.0 | 2.0 | 50 min. | | 11.7 |
| | | | 70 min. | 250 | 5.3 |
| | | 5.0 | 50 min. | | 3.4 |
| | | | 70 min. | 200 | 3.0 |
| Butyraldehydeaniline | 1.0 | 2.0 | 25 min. | 230 | 8.4 |
| | | | 35 min. | | 5.7 |
| | | 5.0 | 15 min. | 200 | 21.7 |
| | | | 25 min. | | 3.8 |
| Mercaptobenzothiazole | 1.0 | 2.0 | 15 min. | 250 | 8.0 |
| | | | 25 min. | | 2.6 |
| | | 5.0 | 15 min. | 200 | 3.2 |
| | | | 25 min. | | 1.2 |
| Dibenzothiazyl disulfide | 1.0 | 2.0 | 20 min. | 230 | 5.0 |
| | | | 40 min. | | 1.2 |
| | | 5.0 | 20 min. | 200 | 3.3 |
| | | | 40 min. | | 1.6 |
| Mercaptobenzothiazole with tetramethylthiuram disulfide | 0.9 MBT 0.1 TMT | 2.0 | 10 min. | 250 | 13.7 |
| | | | 15 min. | | 3.9 |
| | | 5.0 | 10 min. | 230 | 4.8 |
| | | | 15 min. | | 1.3 |

the degradation of the rubber, and the amount of softeners used. The best aging results are obtained when mercaptobenzothiazole or benzothiazyl disulfide are used as accelerators.

#### Bomb-aging to Destruction

| Accelerator | Days in oxygen bomb at 70° C |
|---|---|
| Diphenylguanidine | 14 |
| Butyraldehydeaniline condensation product | 10 |
| Mercaptobenzothiazole | 20 |
| Dibenzothiazyl disulfide | 20 |
| Mercaptobenzothiazole + tetramethylthiuram disulfide | 20 |
| Mercaptobenzothiazole + diphenylguanidine | 14 |
| Ethylideneaniline condensation product | 14 |

Diazoaminobenzene was used as blowing agent

Antioxidants, particularly the phenylnaphthylamines, play a useful part in improving the aging under ordinary conditions. With colored sponge, it is essential that nonstaining antioxidants be used to preserve the brightness of color.

*Latex sponge.*—The accelerators used for the manufacture of latex sponge are all classified in speed as fast, either ultra or semi-ultra. The preparation of this type of sponge in aqueous medium enables these accelerators to be used with safety.

The behavior of the ultra-accelerators under these conditions cannot be forecast, however, from their behavior in dry rubber. As most latex sponge is cured in the form of a wet coagulum, an accelerator is required which is active in slightly aqueous medium. These curing conditions are met most satisfactorily by binary or ternary mixtures based on zinc diethyldithiocarbamate. Good aging and no discoloration can be acquired by suitable choice of accelerator components.

### COLORS

The use of colors is fundamentally to give an attractive or distinctive appearance. Compounds finding general application as rubber colors include organic dyestuffs or their metallic salts, including lakes (available either as such or dispersed in some medium which is easily compounded into rubber), rubber-soluble dyestuffs, and inorganic pigments.

For successful use with sponge, colors must meet the following requirements of manufacture and service: (1) fastness to cure and curing materials, (2) fastness to blowing agents, (3) good aging properties in the sponge, and (4) fastness to conditions of service.

Most colors classified as rubber colors are fast to cure and curing materials, these being normal requirements.

In the presence of blowing agents, which are frequently alkaline, some colors fade or change in shade during vulcanization. Thus, yellow and orange may become redder in shade, and blue may become greener. Fading of colors may be due to the action of light or to the removal of color by bleeding in solutions, such as water, soap water. Boiling with soap solution (2 per cent) may be used as a test to eliminate those colors which are not suitable for toilet sponge, and shows that the majority of colors after vulcanization in sponge bleed into a soap solution. Fortunately there are a few exceptions which are fast, *viz.*, yellow, orange, red, green and blue.

An attractive range is, therefore, available, from which either full tints or pastel shades may be obtained.

Colors unaffected by blowing agents and of a brightness of shade which warrants attention are a much larger group than the really fast colors, and may be used where extraction of the colors by water is not encountered.

When colors are blended, as in browns and some shades of green, the mixtures are resistant to the action of blowing agents only to the same extent as the original colors. Also one or more components may bleed and change the resulting shade of color by partial loss of the original components. Diazoaminobenzene imparts a deep orange shade to sponge mixtures but, at the same time, rich tones can be obtained in mixtures blown with this compound.

*Colors for latex sponge.*—The colors which are fast during the manufacture of press-cured sponge work equally well in the production of latex sponge.

The method of test employed for latex colors consists briefly in the production of rubber sheet containing one per cent of color and subjecting this sheet

to tests under conditions similar to those likely to be encountered in processing and service, *e.g.*, immersion in alkaline and acidic solutions, the effect of solvents used in coagulation (acetone and alcohol), bleeding to white rubber and wrappers, aging to light and weather, and fastness to rubbing.

*Synthetic rubber sponge.*—Associated with thoughts of synthetic rubber sponge are visions of black, oil- and age-resistant, packing sponges, but with Neoprene-GN a series of brightly colored age-resisting sponges can be obtained. The question of accelerators does not arise, as the great point is to delay set-up long enough to enable blowing to take place.

| | | | | |
|---|---|---|---|---|
| Neoprene-GN | 100 | | Neoprene-GN | 100 |
| Light calcined magnesia | 4 | | Light calcined magnesia | 4 |
| Lithopone | 37.5 | | Thermatomic black | 75 |
| Oleic acid | 3 | | Oleic acid | 3 |
| Dibutyl phthalate | 20 | | Dibutyl phthalate | 30 |
| Sodium bicarbonate | 10 | | Sodium bicarbonate | 10 |
| Liquid paraffin | 10 | | Liquid paraffin | 10 |
| Titanium dioxide | 5 | | Zinc oxide | 1 |
| Zinc oxide | 1 | | | |
| Color | as desired | | | |

Cure: 90 min. at 40 lbs. per sq. in. steam pressure.

Good sponge can also be obtained from Neoprenes E and G, but these are not satisfactory for use with colors.

Butadiene interpolymers can be used for the preparation of sponge products, employing tetramethylthiuram disulfide as accelerator and any of numerous fast colors.

In conclusion, the author wishes to express his thanks to Imperial Chemical Industries Limited, in whose Rubber Service Laboratories the work was conducted, and who gave permission for publication.

# EXPERIMENTS ON THE PREPARATION OF TRANSPARENT VULCANIZED RUBBERS *

E. B. JOHNSON AND J. R. SCOTT

## INTRODUCTION

The preparation of transparent rubbers free from bloom and possessing high tensile strength, toughness, and good aging properties is a matter of interest to many branches of the rubber industry, particularly those concerned with fancy goods. The value of transparency as a factor in popularizing rubber goods with the general public has been emphasized by Cotton[1].

As the employment of the usual reinforcing agents in any substantial quantity is ruled out by the condition of transparency, and the sulfur ratio must be kept low to avoid blooming, it is clear that toughness and high tensile strength must be obtained by the use of powerful organic accelerators, all of which require an activator such as zinc oxide to yield their best results. As zinc oxide is a fairly strong pigment, the problem of preparing tough, transparent, accelerated rubbers therefore reduces itself to that of adjusting the zinc oxide content and choosing the accelerator so as to obtain satisfactory activation without undue loss of transparency, or alternatively of finding another activator with less pigmentary effect than zinc oxide. The experiments described below were concerned mainly with the first alternative, as the experiments directed towards the second did not appear promising.

Another way of approaching the problem is by the use of colloidal zinc oxide, of which a very small proportion suffices, presumably because it reacts more quickly with the fat acids[2].

## EXPERIMENTAL

The composition of the mixtures investigated is shown in Tables III and IV. All vulcanizations were made in a daylight press. The mechanical properties

TABLE I

| Mixing | Degree of transparency | | Sulfur bloom | | Tendency to mark | |
|---|---|---|---|---|---|---|
| | ⅔ Optimum cure | Optimum cure | ⅔ Optimum cure | Optimum cure | ⅔ Optimum cure | Optimum cure |
| F | cloudy | clear | none[1] | none | slight | very slight |
| G | slightly cloudy | clear | very slight | none | strong | slight |
| H | clear | clear | very slight | none | medium | medium |
| J | rather cloudy | clear | very slight | none | strong | strong[3] |
| K | cloudy | cloudy | light | slight[2] | strong | strong[3] |

[1] No bloom beyond ⅓ optimum cure.
[2] Persisted up to about 1½ times optimum cure.
[3] Overcured samples marked only slightly.

## TABLE II

### MIXTURE K

| Period of vulcanization (min.) | TS | E 0.5 | PS 400 | Plast. | Scl. |
|---|---|---|---|---|---|
| 15 | 1.88 | 555 | 1.1 | 128 | 86 |
|  | 0.25 | ... | ... | 120 | 72 |
|  | 0.17 | ... | ... | 121 | 68 |
| 23 | 1.92 | 573 | 1.2 | 132 | 86 |
|  | 0.30 | ... | ... | 123 | 69 |
|  | 0.21 | ... | ... | 126 | 65 |
| 30 | 1.79 | 592 | 1.3 | 136 | 85 |
|  | 1.64 | 497 | 2.0 | 128 | 68 |
|  | 0.26 | ... | ... | 133 | 62 |
| 40 | 1.86 | 609 | 0.9 | 138 | 86 |
|  | 1.55 | 535 | 1.5 | 137 | 65 |
|  | 1.26 | 548 | ... | 146 | 62 |
| 50 | 1.82 | 637 | 1.2 | 140 | 84 |
|  | 1.66 | 587 | 2.0 | 144 | 65 |
|  | 1.22 | 577 | ... | 157 | 61 |

(NOTE: The top, middle and bottom figures refer, respectively, to 0, 4, and 10 days of Geer aging.)

## TABLE III

### COMPOSITION OF MIXTURES (PARTS BY WEIGHT)

|  | A | B | C | D | E |
|---|---|---|---|---|---|
| Smoked sheet | 95 | 95 | 95 | 95 | 50 |
| Pale crepe | ... | ... | ... | ... | 50 |
| Sulfur | 2 | 2 | 2 | 1.5 | 1.75 |
| Tetraethylthiuram disulfide | 0.125 | 0.125 | 0.125 | 0.125 | ... |
| Aldehydeammonia | 1 | 1 | 1 | 1 | ... |
| Zinc diethyldithiocarbamate | ... | ... | ... | ... | 0.5 |
| Zinc oxide | 1 | ... | ... | 1 | ... |
| Zinc carbonate | ... | 1.55 | ... | ... | ... |
| Zinc oleate | ... | ... | 7.7 | ... | ... |
| Zinc stearate | ... | ... | ... | ... | 2 |
| Magnesium carbonate | ... | ... | ... | ... | 2 |

## TABLE IV

### COMPOSITION OF MIXTURES (PARTS BY WEIGHT)

|  | F | G | H | J | K | L |
|---|---|---|---|---|---|---|
| Smoked sheet | 100 | 100 | 100 | 100 | 100 | 100 |
| Sulfur | 2 | 2 | 2 | 2 | 2 | 2 |
| Stearic acid | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Zinc oxide | 1 | 1 | 1 | 1 | 1 | ... |
| Diphenylguanidine | 0.5 | 0.5 | 0.5 | ... | ... | ... |
| Mercaptobenzothiazole | 0.5 | ... | ... | ... | 0.5 | ... |
| Tetraethylthiuram disulfide | ... | 0.35 | ... | 0.35 | 0.35 | 0.35 |
| Zinc diethyldithiocarbamate | ... | ... | 0.4 | ... | ... | 0.4 |
| Aldehydeammonia | ... | ... | ... | 1 | ... | ... |

of the vulcanizates are shown in Table V, in which the optimum vulcanization is that giving the best mechanical properties before aging, while $\frac{2}{3}$ of the optimum vulcanizing period represents roughly the degree of vulcanization commonly given in technical practice, though it should be understood that

### TABLE V

| Mixture | T | TS | E 0.5 | PS 400 | Plast. | Scl. |
|---------|---|----|-------|--------|--------|------|
| A | 18(130°) | 1.91 | 630 | 1.6 | 151 | 82 |
|   |          | 1.88 | 635 | 3.0 | 156 | 82 |
| B | 18(130°) | 1.36 | 685 | 2.2 | 173 | 81 |
|   |          | 1.36 | 745 | 3.3 | 178 | 82 |
| C* | 70(130°) | ... | ... | ... | ... | .. |
|   |          | 0.9 | 930 | 8.5 | 197 | 69 |
| D | 10(130°) | 1.82 | 616 | 1.5 | 140 | 90 |
|   |          | ... | ... | ... | ... | .. |
| E | 13(126°) | 0.86 | 870 | 2.95 | 143 | 68.5 |
|   |          | 0.83 | 890 | 3.0 | 138 | 69.5 |
| F | 28(122°) | 2.13 | 540 | 1.3 | 133 | 81 |
|   |          | 2.11 | 580 | 1.6 | 138 | 80.5 |
| G | 27(122°) | 2.18 | 525 | 1.0 | 118 | 79.5 |
|   |          | 2.00 | 560 | 1.1 | 119 | 82 |
| H | 11(122°) | 2.14 | 537 | 1.9 | 121 | 80 |
|   |          | 2.16 | 573 | ... | ... | .. |
| J | 8(122°) | 1.96 | 572 | 1.6 | 124 | 78 |
|   |          | 1.95 | 585 | ... | ... | .. |
| K | 20(122°) | 1.96 | 566 | 1.5 | 130 | 79.5 |
|   |          | 1.90 | 560 | ... | 128 | 79 |
| L | 5(122°) | 0.50 | 1100 | 3.9 | 194 | 71 |
|   |          | ... | ... | ... | ... | .. |

(NOTE: The upper and lower figures refer, respectively, to optimum and ⅔ optimum cures.)

\* Vulcanizing was continued up to 50 min., but the rubber was still undercured; the time of optimum cure is, therefore, only approximate.

this is not necessarily the best cure for specialized types of rubber such as those now under discussion. The following abbreviations are used in the tables:

T = optimum period of vulcanization (min.); vulcanizing temperature (° C) is given in brackets.

TS = tensile strength (kg. per sq. mm.).

E 0.5 = elongation (percentage under a load of 0.5 kg. per sq. mm.).

PS 400 = permanent set (percentage after stretching to 400% elongation for 15 min., and allowing to recover for 60 min.).

Plast. = plastometer hardness number.

Scl. = resilience by scleroscope.

### 1. COMPARISON OF ZINC OXIDE, ZINC CARBONATE, AND ZINC OLEATE AS ACTIVATORS

As it is usually considered that zinc oxide must be converted into a soap (fat acid salt) before it can activate the accelerator, the use of a zinc soap instead of the oxide is clearly a possible method of avoiding the pigmenting effect associated with the oxide. Zinc carbonate has been suggested as an activator because it is a weaker pigment than the oxide, and would presumably be converted into a soap by the resin acids. Experiments were therefore made to compare the activating effects of zinc oxide, carbonate, and oleate.

The choice of an accelerator for these experiments was based on previous tests with a large number of accelerators[3]. These tests indicated that tetraethylthiuram disulfide is the best accelerator for giving good mechanical properties with a low sulfur ratio and for yielding vulcanizates with low free sulfur

content. In these experiments, made with a mixing containing 3 per cent zinc oxide, the accelerators were found to differ greatly in regard to the opacity of the vulcanizate, aldehydeammonia and thiocarbanilide giving the least opaque rubbers. As thiocarbanilide is less active than aldehydeammonia and is troublesome owing to its scorching tendency, it was decided to use aldehyde-ammonia and tetraethylthiuram disulfide together, with a view to obtaining transparency and freedom from bloom.

A first trial mixing with 2 per cent of zinc oxide was not sufficiently transparent, and in subsequent experiments the proportion was therefore reduced to about 1 per cent on the rubber. Mixtures A, B, and C were then made, containing respectively zinc oxide, zinc carbonate, and zinc oleate in such proportions as to contain equal amounts of zinc (see Table III).

Replacing zinc oxide by the carbonate did not appreciably alter the rate of vulcanization, but gave a much weaker, softer rubber, with higher permanent set (see Table V). The zinc carbonate rubber was more transparent than that containing zinc oxide, and was indistinguishable in appearance from a pure rubber-sulfur mixture made with the same smoked sheet. Seven weeks after vulcanizing, however, the optimum-vulcanized zinc carbonate rubber had developed a fairly pronounced bloom, and even overvulcanized samples had bloomed slightly. The zinc oxide mixture at optimum cure showed only a light bloom. Zinc carbonate therefore does not appear promising as an activator for use in nonblooming rubbers. As the optimum vulcanizing period was the same with both zinc oxide and zinc carbonate, being probably determined by the limited period of activity of the fugitive accelerator tetraethylthiuram disulfide, the heavier bloom and inferior mechanical properties of the zinc carbonate rubber may be taken as evidence that the carbonate was less active than the oxide in indirectly promoting (through the medium of the accelerator) the reaction between rubber and sulfur.

The zinc oleate mixture was unsatisfactory, for vulcanization was relatively very slow, and the vulcanizates were weak and flabby, and soon developed a heavy bloom. It is evident that the large amount of oleate acted as a softener and also retarded the rubber-sulfur reaction. It would have been more logical to add a proportion of zinc oleate equivalent to the normal fat acid content of raw rubber, since this is the maximum amount of zinc soap which could be formed from zinc oxide during vulcanization. The subject was not investigated further, however, for meantime satisfactory results were obtained with zinc oxide.

Mixture A was found to possess very good aging properties, as is shown by the following tensile figures obtained before and after 3 years' natural aging in darkness.

| Period of vulcanization | 19 min.* | 45 min. |
|---|---|---|
| Tensile strength before aging | 1.87 | 1.57 |
| Tensile strength after aging | 1.90 | 1.75 |

* optimum vulcanization.

## 2. Nonblooming Modification of Zinc Oxide Mixture

The chief defect in mixture A was its tendency to bloom. The effect of reducing the sulfur content from 2.0 to 1.5 per cent was therefore tried (mixture D). The reduction in sulfur produced very little change in mechanical properties except an increase in resilience, doubtless due to the shorter vulcanization with the lower sulfur ratio. As mixtures A and D were made at

widely separated times, the quicker vulcanization of D may have been due to variation in experimental conditions rather than to a real difference between the two mixtures.

The new mixture D was more transparent than that with 2 per cent sulfur, and was superior in this respect even to a 95 : 5 rubber-sulfur mixture made with the same raw rubber, for when viewed by transmitted light, it showed a clear brown color of a lighter shade than that of the rubber-sulfur mixture. After $2\frac{1}{2}$ years, no trace of bloom had appeared on the optimum-vulcanized sample D. As the range of samples did not include one vulcanized much below the optimum cure, it cannot be said whether bloom would have appeared at $\frac{2}{3}$ optimum cure.

No material was available for tensile tests after aging, but after $2\frac{1}{2}$ years' storage in darkness, all the rubbers, including grossly overcured samples (up to $4\frac{1}{2}$ times the optimum cure), were in excellent condition, judged by hand. The aging results for this mixture and for mixture A show that rubbers of this type can be fully vulcanized, so as to assure the absence of blooming, without incurring the danger of bad aging properties.

### 3. Mixture with Zinc Stearate and Magnesium Carbonate

Cotton[1] gives a mixture containing zinc stearate and magnesium carbonate as joint activators for zinc diethyldithiocarbamate which is stated to vulcanize in 5 minutes at 126° C, giving a good transparent rubber. It may be noted further that the preparation of transparent rubbers by means of zinc dialkyl-dithiocarbamate accelerators without addition of a zinc activator has been patented[4]. Mixture E was therefore examined. It was identical to Cotton's mixing except for a slightly lower sulfur content, which was deemed advisable because 2 per cent sulfur in mixture A led to blooming. A mixture of crepe and smoked sheet was used, with the object of producing a vulcanizate of a medium brown color.

Table V shows that mixture E was considerably inferior in mechanical properties to mixtures A, B and D and to F, G, H, J and K (described below), all of which contained zinc oxide as activator. At both optimum and $\frac{2}{3}$ optimum cures, the rubber had a clear brown color considerably lighter than that of the smoked sheet mixtures A, B and D; the $\frac{2}{3}$ optimum cure, however, soon developed a slight bloom. In view of these results, it was decided to use zinc oxide as activator in subsequent experiments.

### 4. Mixtures with Various Accelerators

The main object of this series of experiments was to obtain the greatest possible tensile strength and toughness by the aid of combinations of accelerators, taking advantage of the two-accelerator effect to obtain better results than would be obtained by one accelerator alone. These experiments are of particular interest in connection with transparent cycle tire treads, where great strength and toughness are required to resist abrasive wear.

One reason for trying accelerator combinations without aldehydeammonia was the fact that this accelerator gave a marked unpleasant smell to the vulcanizate; this would be a serious disadvantage for certain applications of transparent rubbers.

Mixtures F, G, H, J and K, containing various combinations of accelerators, were therefore tested. In connection with F, it may be noted that a compound

of diphenylguanidine and mercaptobenzothiazole has been patented as an accelerator[5]. The Goodyear patent claims also the use of the constituent accelerators added as such to the mix.

*Properties before Aging (see Table V)*: All five mixtures vulcanized very rapidly at 122° C, and gave excellent mechanical properties, superior in this respect to the previous mixtures A and D, especially with regard to stiffness and hardness.

It is interesting to note the proportions of the usual reinforcing agents which would be required to give rubbers of the same stiffness and hardness as mixtures F to K. To give an elongation at 0.5 kg. per sq. mm. of 550 per cent, and plastometer hardness = 125, approximately the following quantities would have to be added to 100 parts of 95 : 5 rubber-sulfur stock:

|  | Gas black | Magnesium carbonate | Zinc oxide |
|---|---|---|---|
| Parts by weight | 10 | 22 | 65 |
| Permanent set (percentage) after 400% elongation | 2.0 | 10 | 6 |

An important characteristic of the accelerated mixtures is that the permanent set after 400 per cent elongation is low (1.0 to 1.9 per cent) compared with that of the mixtures reinforced to the same degree of stiffness and hardness by means of inorganic substances, especially zinc oxide and magnesium carbonate. Moreover, inorganic substances tend to lower the resilience, whereas accelerators improve this property. In these respects, therefore, organic accelerators have an advantage over inorganic reinforcing agents as a means of increasing rigidity without impairing other elastic properties.

The appearance of the accelerated rubbers 6 months after vulcanizing is indicated in Table I. All the rubbers had the dark brown color characteristic of a rubber—sulfur mixture made from smoked sheet, with the exception of the undercured samples of F, which showed evidence of pigmentation by zinc oxide. When viewed by transmitted light, however, some of the rubbers showed a cloudiness, usually patchy; whereas others were quite clear, as indicated in the table. Compared with a 95 : 5 rubber-sulfur mixture made from the same smoked sheet, mixtures F, G, H and K had a considerably lighter brown color by transmitted light; J was darker than these four, but lighter than the rubber-sulfur mixture. It should be added that the smoked sheet used in these experiments vulcanized unusually slowly in the 95 : 5 mixture. As rubber darkens with advancing vulcanization, the superiority of the accelerated mixtures over the 95 : 5 mixture as regards color might not have been so pronounced if normal smoked sheet had been used. It is obvious, nevertheless, that accelerated rubbers containing sufficient zinc oxide for activation can be made as transparent as mixtures containing only rubber and sulfur.

It was noticed that some of the rubbers became marked very easily when scratched with a hard object, light brown or grayish streaks being produced, apparently owing to an efflorescence of accelerator on the surface. The degree of this tendency to mark is indicated in Table I.

*Aging Properties*: Mixtures F, G and K were repeated for the purpose of making Geer aging tests, the mechanical properties being examined before aging and after periods of 4 and 10 days at 70° C (see Table VI). Mixture F aged remarkably well, and G was quite satisfactory. The results for K were unusual in that the optimum and ⅔ optimum cures aged badly, whereas overcured samples aged much better. This is shown by the figures for the whole set of samples (Table II).

### TABLE VI

| | TS | | E 0.5 | | PS 400 | | Plast. | | Scl. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ⅔ | opt. | ⅔ | opt. | ⅔ | opt. | ⅔ | opt. | ⅔ | opt. |
| F | 1.96 | 2.12 | 568 | 550 | 1.25 | 1.2 | 134 | 132 | 82 | 82 |
| | 2.39 | 2.33 | 515 | 500 | 1.8 | 1.7 | 130 | 129 | 77 | 75 |
| | 2.24 | 2.22 | 525 | 520 | 1.7 | 1.2 | 135 | 135 | 70 | 68 |
| G | 2.16 | 2.28 | 565 | 535 | 1.3 | 1.1 | 121 | 122 | 88 | 88 |
| | 2.16 | 2.12 | 478 | 485 | 1.4 | 1.7 | 129 | 130 | 74 | 73 |
| | 1.30 | 1.20 | 520 | 525 | 1.7 | 1.9 | 151 | 157 | 66 | 65 |
| K | 1.84 | 1.91 | 554 | 562 | 1.2 | 1.2 | 128 | 130 | 83 | 83 |
| | 0.24 | 0.28 | ... | ... | ... | ... | 118 | 120 | 72 | 71 |
| | 0.17 | 0.18 | ... | ... | ... | ... | 121 | 123 | 68 | 67 |

(NOTE: Upper, middle and bottom figures refer, respectively, to 0, 4, and 10 days' aging; opt. = optimum cure; ⅔ = ⅔ optimum cure.)

This improvement in aging with overcure is the exact opposite of what is usually observed. The results were, however, confirmed by hand tests on the first set of vulcanizates made from mixture K (no rings were available for exact tensile tests). After 9 days in the Geer oven, the 20-minute vulcanizate was quite weak, the 30-minute vulcanizate fairly weak, and the 38- and 45-minute vulcanizates were still strong.

### 5. MIXTURE WITHOUT ACTIVATOR

In the discussion on a paper dealing with superaccelerators, Naunton[6] stated that tetraethylthiuram disulfide could function in the same way as zinc oxide towards zinc diethyldithiocarbamate, so that a combination of these two accelerators should presumably give satisfactory vulcanization without zinc oxide. Mixture L was, accordingly, prepared to test this point. Although vulcanization was extremely rapid, the mechanical properties of the vulcanizates were very poor, and a heavy bloom soon developed, even on very much overcured samples. It is evident that the rate of combination of rubber and sulfur must have been too slow to give a good vulcanizate before the accelerators were rendered inactive.

### SUMMARY AND CONCLUSION

1. It has been found possible, by the use of combinations of organic accelerators, to prepare accelerated rubbers which contain sufficient zinc oxide for activation but show no trace of pigmentation by the oxide, and are quite as transparent as a mixture containing only rubber and sulfur, and often lighter in color than the latter mixture. These accelerated rubbers have excellent tensile properties. The aging properties vary considerably according to the accelerators used, but in most cases are very good, even if the rubber is overcured. It is, therefore, possible to make nonblooming rubbers without danger of bad aging.

2. Tests with other activators (zinc carbonate, zinc oleate, and zinc stearate plus magnesium carbonate) showed that these are less effective than zinc oxide, for the vulcanizates obtained had inferior mechanical properties and, in the case of zinc carbonate and oleate, showed a strong tendency to bloom.

3. A combination of accelerators which has been stated to work well without activator was shown to vulcanize very quickly, but to give poor mechanical properties.

4. The tendency of various accelerators to give rubbers, the surfaces of which are easily marked by scratching, presumably owing to efflorescence of accelerator, was noted.

5. The most promising of the mixtures tested for making transparent vulcanized rubbers was one accelerated with diphenylguanidine plus mercapto-benzothiazole, with zinc oxide as activator (mixture F).

6. A mixture is described (mixture K) which gives better aging when vulcanized beyond the optimum tensile properties than when vulcanized short of the optimum cure.

7. Rubbers can be toughened by the use of organic accelerators so as to possess greater resilience and lower permanent set than if toughened by the usual inorganic reinforcing agents.

The aging tests described above were all made in the absence of light. For transparent rubber goods which are exposed to light during use, the addition of antioxidants and (or) softeners might be found necessary to give resistance to deterioration by light. In connection with fancy goods, the staining of paper in contact with the rubber may be of importance, and in such cases the choice of accelerators and antioxidants must be made with this in mind. The staining effects of numerous accelerators and antioxidants have already been described[7].

In conclusion, it should be added that the experiments were directed in the first instance towards the production of brown transparent rubbers, for which reason smoked sheet was used. Where a light-colored vulcanizate is required, and especially when it is desired to obtain colored rubbers by adding organic dyes, the use of pale crepe is essential.

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# EFFECT OF TEMPERATURE AND PRESSURE
## ON OXYGEN PRESSURE AGING *

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An increase in the temperature of the oxygen pressure test from 70° to 80° C greatly increases the rate of aging of rubber vulcanizates. The temperature coefficients of aging rate for the six stocks tested vary between 1.63 and 3.48. The state of cure markedly affects the temperature coefficient of some stocks. It is obvious that no change in the specification from 70° to 80° C should be made without first determining the temperature coefficient of the stock involved.

A decrease in the pressure of the oxygen pressure test decreases the rate of aging, but the rate is not proportional to pressure. The relative rates of aging between 0.5 and 300 pounds oxygen pressure for the stocks tested vary between 1.09 and 4.87 for the normal cures, and between 1.50 and 6.74 for the longer cures. The state of cure markedly affects the change in rate of aging with change in pressure.

The data show that changes in the pressure of the oxygen pressure test must be accompanied by a revision of all aging specifications, which will involve an individual study of each stock and every cure of each stock, since no correlation between stocks seems to exist for the changes in rate of aging that occur with changes in pressure.

The oxygen pressure test at 70° C and 300 pounds per square inch oxygen pressure has proved a valuable tool in the hands of the rubber technologist for evaluating the age resistance of rubber vulcanizates. With the development of modern accelerators and antioxidants, however, the test has been considered too slow for many purposes; as a result there has been considerable agitation for more rapid methods of testing, directed principally toward changing the conditions of the oxygen pressure test. The simplest of these proposed changes consists in raising the temperature at which the test is carried out; changes in pressure have also been suggested.

A certain amount of work on the effects of changing the temperature and pressure in the oxygen pressure test has already been reported. Morgan and Naunton[1] found that the temperature coefficient of the oxidation of rubber varies with the nature of the stock and with the antioxidant used, and concluded that measurements at one temperature will not give a true indication of the relative rates of oxidation of different stocks at another temperature. These workers also report that oxidation is different above 80° C than it is at lower temperatures. Williams and Neal[2] found that, in the neighborhood of 70° C, a second type of oxidation reaction seems to become evident. They also report that decrease in tensile strength is not proportional to the oxygen pressure at 50° C, and warn against the use of higher temperatures and pressures in aging tests if a close relation to natural aging is to be maintained. Yamazaki and Okuyama[3] followed the oxidation of rubber stocks by the acetone extraction method, and found a marked difference between oxidation at 70° and 90° C. Davey[4] points out the differences in oxidation at 70° and

100° C. Ingmanson and Kemp[5] report that changes in oxygen pressure at 70° C affect different stocks differently, and that the same is true to a smaller extent of differences in temperature; but these authors recommend 50 pounds oxygen pressure and 80° or 85° C as conditions for the oxygen pressure test. Kemp[6] shows a change in oxidation above 90° C, and warns against changing the temperature specifications of aging tests without obtaining proper correlation with service conditions. The work of Booth and Beaver[7] shows a variation in the aging of a single stock in a number of the standard tests. Numerous workers have pointed out a lack of correlation between natural and artificial aging[8] and between different conditions of artificial aging[9]. On the other hand, Nagai[10] reports that there is little difference between aging at 55°, 70°, 85°, and 100° C. Dufraisse[11] finds satisfactory correlation between aging in the Geer oven and oxidizability at 80° and 120° C. Kohman[12] reports that aging at 80° C corresponds closely to natural aging, and Follansbee[13] found a correlation between the 70° C oven and shelf aging.
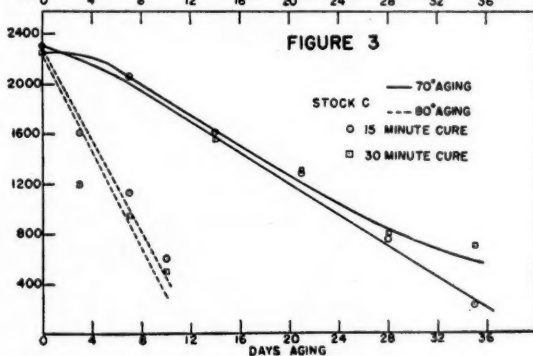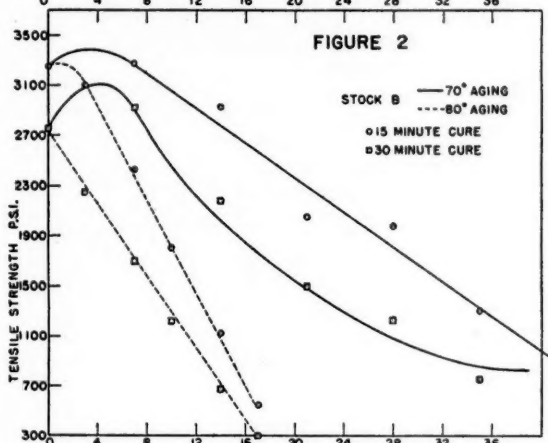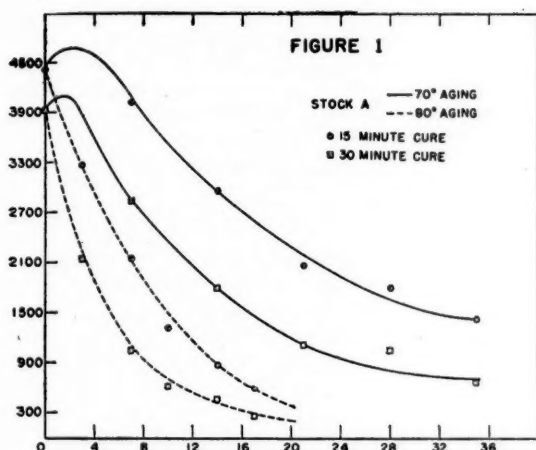
Much of this previous work involved the use of oxygen adsorption as one measure of the extent of deterioration, and this was compared to changes in physical properties as judged by loss in tensile strength. Since the conventional oxygen pressure test compares changes in tensile strength with time of aging rather than with the extent of chemical attack, the work reported in this paper was initiated to study the effect of temperature and pressure changes on the test, as determined by the conventional methods of evaluation.
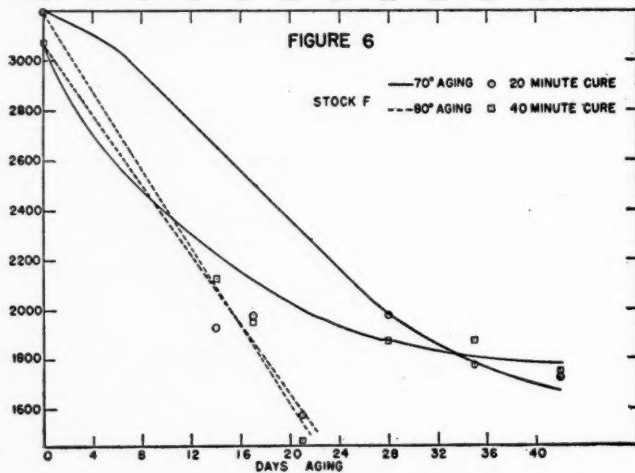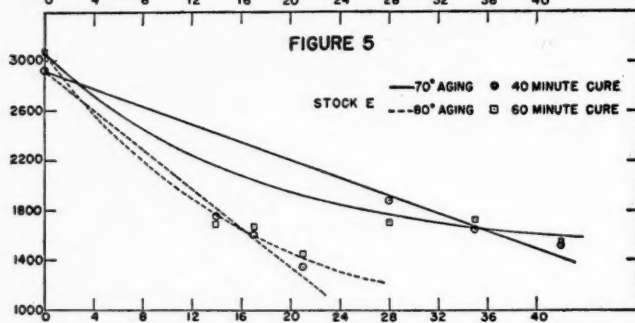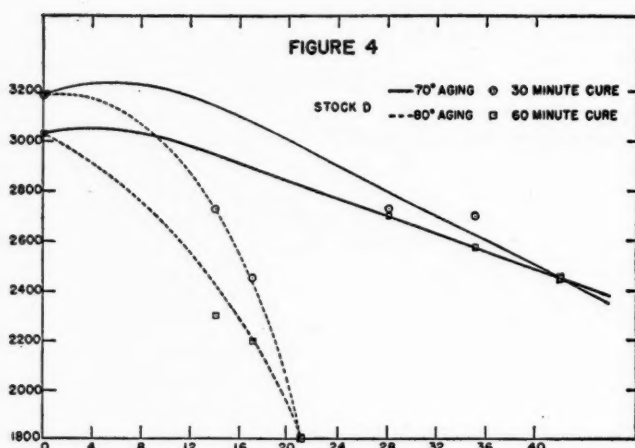
### TABLE I
### STOCK RECIPES

| Stock | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| Smoked sheet | 100.0 | 100.0 | 100.0 | 100.0 | ... | ... |
| Neoprene Type E | ... | ... | ... | ... | 100.0 | ... |
| Neoprene Type GN | ... | ... | ... | ... | ... | 100.0 |
| Zinc oxide | 5.0 | 5.0 | 5.0 | 5.0 | 10.0 | 10.0 |
| Kalvan | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 |
| Stearic acid | 1.0 | 1.0 | 1.0 | 1.0 | ... | ... |
| Neozone-A | 1.0 | 1.0 | ... | ... | 2.0 | 2.0 |
| Akroflex-C | ... | ... | ... | 1.0 | ... | ... |
| Thermoflex-C | ... | ... | ... | 1.0 | ... | ... |
| Zenite | ... | ... | 1.25 | ... | ... | ... |
| Zenite-A | ... | 1.25 | ... | ... | ... | ... |
| Thionex | ... | ... | 0.1 | 3.5 | ... | ... |
| Accelerator 80S | 1.0 | ... | ... | ... | ... | ... |
| Tetrone-A | ... | ... | ... | 1.0 | ... | ... |
| Telloy | ... | ... | ... | 3.0 | ... | ... |
| Litharge | ... | ... | ... | 0.5 | ... | ... |
| Latac | ... | ... | ... | ... | ... | 0.25 |
| Extra-light calcined magnesia | ... | ... | ... | ... | 5.0 | 4.0 |
| FF wood rosin | ... | ... | ... | ... | 5.0 | ... |
| Sulfur | 2.5 | 2.0 | 1.0 | ... | ... | ... |
| Cure    Minutes | 15, 30 | 15, 30 | 15, 30 | 30, 60 | 40, 60 | 20, 40 |
|          Temp. (° F) | 287 | 287 | 287 | 274 | 307 | 307 |

The stocks chosen for study are listed in Table I. All of them contained 25 parts of Kalvan in addition to the necessary curatives. It was thought that a lightly loaded stock would give somewhat more uniform results than either a pure gum compound or one containing a large proportion of filler.

The acceleration of the stocks was varied to cover a wide range of typical accelerations used by the industry. Stocks A and B are normal sulfur com-

FIGURE 1

STOCK A — 70° AGING --- 80° AGING ● 15 MINUTE CURE ▫ 30 MINUTE CURE

FIGURE 2

STOCK B — 70° AGING --- 80° AGING ○ 15 MINUTE CURE ▫ 30 MINUTE CURE

TENSILE STRENGTH P.S.I.

FIGURE 3

STOCK C — 70° AGING --- 80° AGING ○ 15 MINUTE CURE ▫ 30 MINUTE CURE

DAYS AGING

FIGURE 4

STOCK D

—— 70° AGING   ⊙  30 MINUTE CURE
--- 80° AGING   ▢  60 MINUTE CURE

FIGURE 5

STOCK E

—— 70° AGING   ●  40 MINUTE CURE
--- 80° AGING   ▣  60 MINUTE CURE

FIGURE 6

STOCK F

—— 70° AGING   ⊙  20 MINUTE CURE
--- 80° AGING   ▢  40 MINUTE CURE

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pounds accelerated by an aldehydeamine and an activated thiazole, respectively. Stock C is a low-sulfur heat-resisting compound. The antioxidant was omitted to see if it aged as well as normal sulfur stock B with an antioxidant. D is typical of the no-added-sulfur stocks used in the wire industry. Such stocks have excellent heat resistance and resistance to oxygen bomb aging. Neoprene stocks E and F were included as typical nonrubber elastomers. The short cures on all these stocks are considered good technical cures, while the longer cures are overcures.

## COMPARISON OF AGING AT 70° AND 80° C

To determine the effects of changing the temperature, the stocks in Table I were aged at 70° and 80° C, under 300 pounds oxygen pressure. In Figures 1 to 6 the time of aging is plotted against the tensile strength. From a consideration of these curves it is obvious that aging at 80° C is considerably faster than aging at 70°, and also that the different stocks react differently to this change in temperature.

The effects of changing the temperature may be considered in more detail by a study of the relative rates of aging. One method is to compare the times required for the tensile strengths of the different stocks to drop to 50 per cent of the original tensile. For a given stock, then, aging at the two temperatures is compared over exactly the same range of tensile strength. The times, $T'$, required to reach 50 per cent deterioration are listed in Table II. This table

### TABLE II
#### TIME AND RELATIVE RATE OF AGING REQUIRED TO REACH 50 PER CENT DETERIORATION

| Stock | Time of cure (min.) | $T'_{70°}$ (days) | $T'_{80°}$ (days) | $R'$ |
|-------|---------------------|-------------------|-------------------|------|
| A | 15 | 21.9 | 7.0 | 3.13 |
|   | 30 | 11.8 | 3.4 | 3.47 |
| B | 15 | 31.0 | 11.2 | 2.77 |
|   | 30 | 22.1 | 9.2 | 2.40 |
| C | 15 | 20.1 | 5.9 | 3.41 |
|   | 30 | 21.7 | 5.6 | 3.88 |
| D | 30 | 52.0 | 18.9 | 2.75 |
|   | 60 | 56.0 | 17.2 | 3.25 |
| E | 40 | 39.8 | 18.0 | 2.21 |
|   | 60 | 42.4 | 18.9 | 2.24 |
| F | 20 | 34.6 | 17.8 | 1.95 |
|   | 40 | 41.0 | 18.0 | 2.28 |

also contains the relative rate of aging, $R'$, at 80° C, compared to that at 70°. $R'$ is obtained by the expression:

$$R' = T'_{70°}/T'_{80°}$$
$$\text{where } T' = \text{time (days)}$$

Because of the initial rise in the time-tensile curves of some of the stocks, this method may not be entirely satisfactory. To overcome this difficulty, similar calculations of the rate were made using, instead of a 50 per cent decrease in tensile, an arbitrary decrease in tensile, usually 1000 pounds per square inch,

## TABLE III
### RELATIVE RATES OF AGING

| Stock | Time of cure (min.) | $T_{70°}$ (days) | $T_{80°}$ (days) | Drop in tensile (lb./sq. in.) | $R$ |
|-------|---------------------|------------------|------------------|-------------------------------|-----|
| A | 15 | 7.9 | 3.4 | 3400–2400 | 2.33 |
|   | 30 | 6.1 | 2.4 | 3300–2300 | 2.54 |
| B | 15 | 14.5 | 5.3 | 2900–1900 | 2.74 |
|   | 30 | 12.5 | 7.0 | 2300–1300 | 1.79 |
| C | 15 | 16.1 | 5.4 | 2000–1000 | 2.98 |
|   | 30 | 16.5 | 5.2 | 1950– 950 | 3.17 |
| D | 30 | 32.4 | 9.3 | 3000–2200 | 3.48 |
|   | 60 | 34.2 | 10.3 | 2800–2200 | 3.32 |
| E | 40 | 28.0 | 12.2 | 2700–1700 | 2.30 |
|   | 60 | 36.2 | 13.2 | 2600–1600 | 2.74 |
| F | 20 | 20.7 | 12.7 | 3000–2000 | 1.63 |
|   | 40 | 24.5 | 14.2 | 2900–1900 | 1.73 |

over the smooth part of the curve. These relative rates are listed in Table III; $T$ is the time required to decrease the tensile strength over the range indicated in the column headed "Drop in tensile", and $R$ is the relative rate obtained by the equation:

$$R = T_{70°}/T_{80°}$$

Since $R$ in Table III is the relative rate of aging between 70° and 80° C, it is actually the temperature coefficient of aging. For a normal chemical reaction, the temperature coefficient is usually between 2.0 and 3.0. For the stocks tested here, the values range between 1.63 and 3.48. It would appear from a consideration of the four rubber stocks tested that, for a normal cure, the temperature coefficient is larger for the better aging stocks. The same is true for the two Neoprene stocks (E and F). The practical importance of these facts may be illustrated by an example: If the Neoprene Type GN stock (F) were found to meet aging specifications at 70° C for a certain purpose and if, to speed up the test, the specifications were changed to 80° C, the test would require only 61.4 per cent as long. That is, if the specifications call for 20.7 days of aging at 70° C, only 12.7 days will be required at 80°. If the Neoprene Type E stock (E) is to meet a different set of 70° specifications which call for 28.0 days of aging, and the test is speeded up by raising the temperature to 80°, it would be expected that only 61.4 per cent of 28.0 days would be required at 80° to produce the corresponding deterioration. That is, the specifications, changed to 80° C, would call for 17.2 days of aging. Although the Neoprene Type E stock (E) would meet the specifications at 70° C, it would fall far short of meeting them after they were changed to 80° C, on the basis of results with the Neoprene Type GN stock (F), because after 12.2 days stock E would have deteriorated as much at 80° as it would after 28.0 days at 70°. Thus a stock which had given satisfactory results in service would be rejected if the specifications were arbitrarily changed. Conceivably a stock might fail to meet the specifications at 70° C, but might easily meet the revised specifications at 80° if the correct temperature coefficient was not used.

The state of cure also markedly affects the temperature coefficient of aging. Table IV shows the percentage change in the values of $R'$ and $R$ in going from the short to the longer cure.

TABLE IV

EFFECT OF TIME OF CURE ON TEMPERATURE COEFFICIENT OF AGING

| Stock | Time of cure (min.) | $R'$ | % Change in $R'$ | $R$ | % Change in $R$ |
|-------|---------------------|------|------------------|-----|-----------------|
| A | 15 | 3.13 | | 2.33 | |
|   | 30 | 3.47 | 11.0 | 2.54 | 9.0 |
| B | 15 | 2.77 | | 2.74 | |
|   | 30 | 2.40 | −13.5 | 1.79 | −34.5 |
| C | 15 | 3.41 | | 2.98 | |
|   | 30 | 3.88 | 13.5 | 3.17 | 6.5 |
| D | 30 | 2.75 | | 3.48 | |
|   | 60 | 3.25 | 18.0 | 3.22 | −4.5 |
| E | 40 | 2.21 | | 2.30 | |
|   | 60 | 2.24 | 1.5 | 2.74 | 19.0 |
| F | 20 | 1.95 | | 1.63 | |
|   | 40 | 2.28 | 17.0 | 1.73 | 6.0 |

A large change in temperature coefficient $R$ is observed with only two of the stocks. Doubling the time of cure of the normal sulfur stock accelerated with a thiazole (B) decreases the effect of change in temperature markedly, while increasing the time of cure of the Neoprene Type E stock (E) causes a large increase in the temperature coefficient. If $R'$, based on a 50 per cent decrease in tensile strength is considered, there is an appreciable increase in temperature coefficient in all cases except stocks B and E. With stock B, there is again a decrease in the temperature coefficient at the longer cure, but with stock E there is very little change. The results are that, if stock B is overcured, it appears better at 80° C compared to the other stocks. The same is true of stock E, but to a lesser extent.
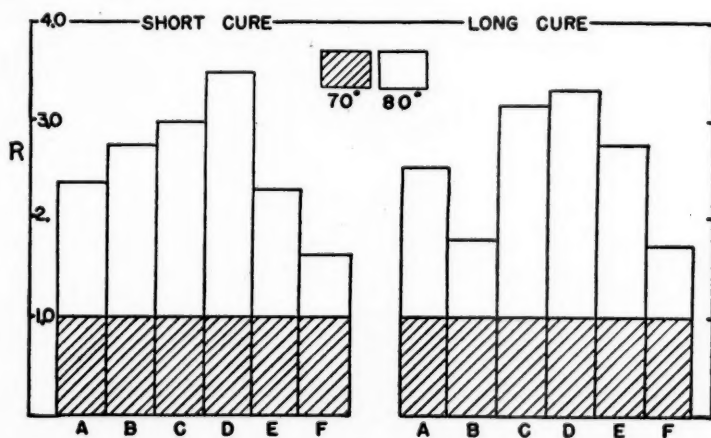


FIG. 7.—Differences in relative rates of aging.

Figure 7 is a graphic representation of the data, and brings out clearly the large differences in the relative rates of aging.

### EFFECT OF OXYGEN PRESSURE ON AGING AT 80° C

To determine the effect of changing the pressure in the oxygen pressure test, the stocks in Table I were aged at 0.5, 50, 150, and 300 pounds per square inch at 80° C.   The absolute pressures corresponding to these gauge pressures and the ratio of these absolute pressures follow:

|                           | Pounds per square inch |        |        |        |
|---------------------------|:----:|:----:|:-----:|:-----:|
| Gauge pressure            | 0.5  | 50   | 150   | 300   |
| Absolute pressure         | 15.2 | 64.7 | 164.7 | 314.7 |
| Ratio of absolute pressure| 1    | 4.25 | 10.8  | 20.7  |

The data[1] obtained from these experiments are plotted in Figures 8 to 19. These curves show that the rate of aging increases with increasing oxygen pressure, and that the rate of increase is not proportional to the change in pressure.

The rates of aging, $R'$, of these stocks at the different pressures were calculated by comparing the times required to reach approximately 50 per cent of the original tensile strength:

$$R' = T_1/T_2$$

where $T_1$ = time required for tensile strength to decrease to approximately
        50 per cent of original, at 0.5 lb. gauge pressure
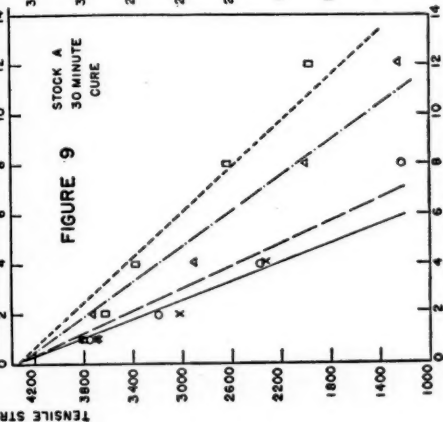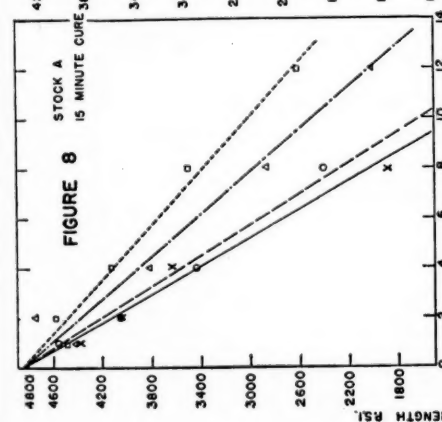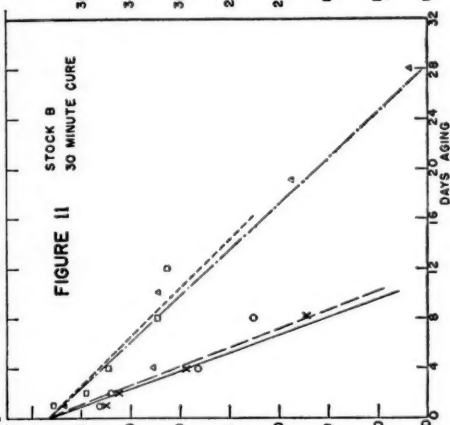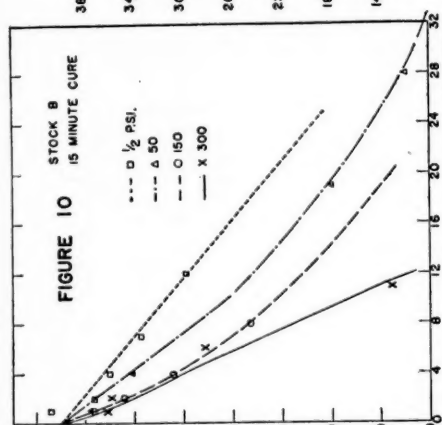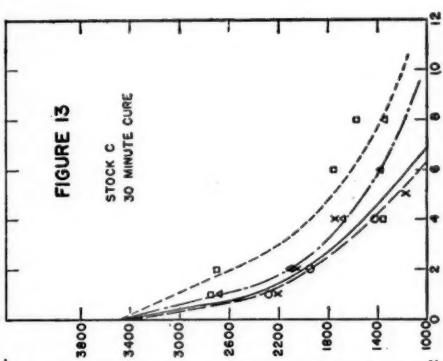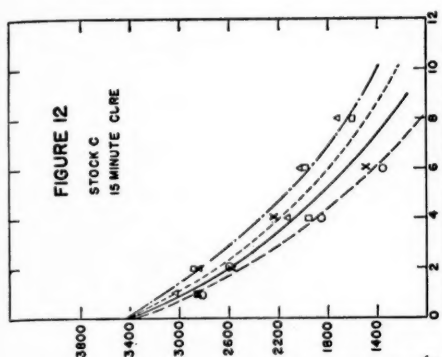    $T_2$ = corresponding time for higher pressures
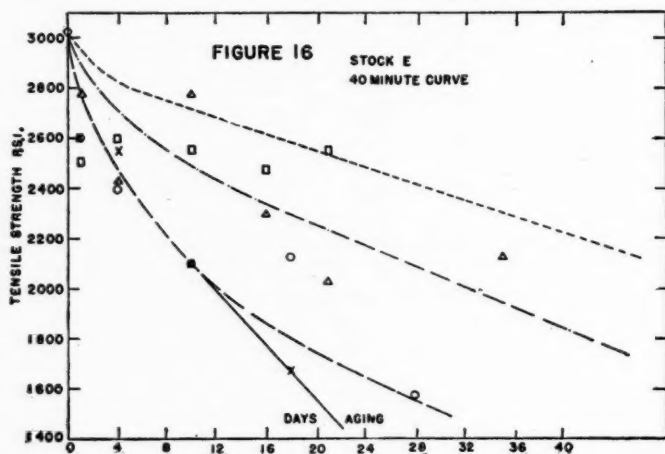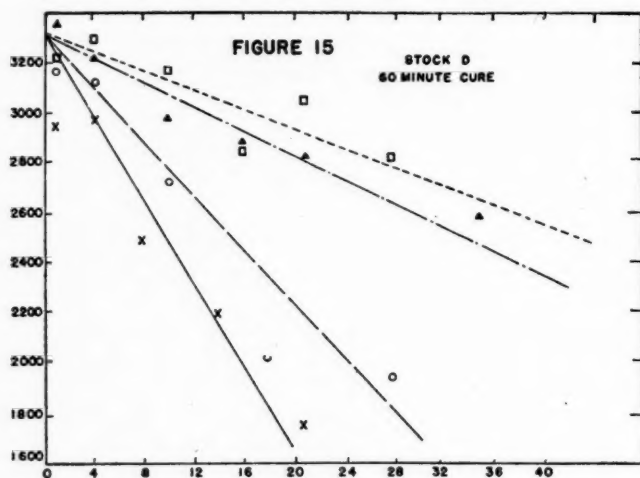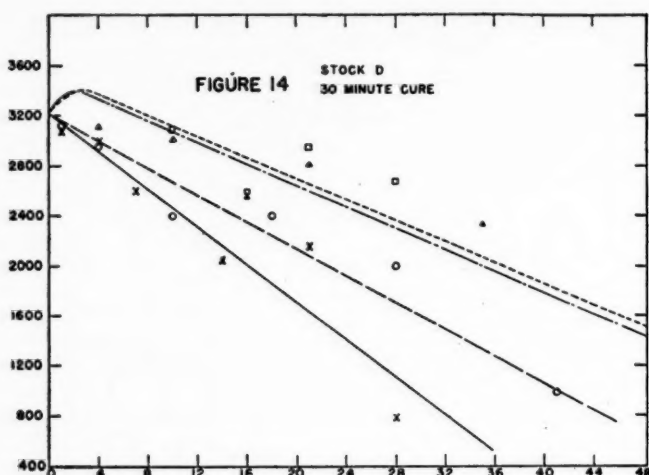
The values of $R'$ are given in Table V.

### TABLE V

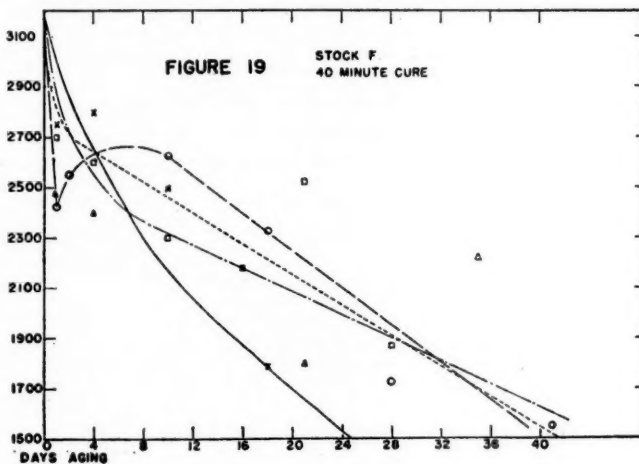EFFECT OF INCREASING PRESSURE ON RELATIVE AGING RATE

| Stock | Time of cure (min.) | $R'$ at gauge pressure of: | | | |
|:---:|:---:|:---:|:---:|:---:|:---:|
|     |     | 0.5 | 50 | 150 | 300 |
| A   | 15  | 1 | 1.27 | 1.76 | 1.94 |
|     | 30  | 1 | 1.29 | 2.00 | 2.35 |
| B   | 15  | 1 | 1.39 | 1.95 | 2.79 |
|     | 30  | 1 | 1.06 | 2.52 | 2.75 |
| C   | 15  | 1 | 0.85 | 1.31 | 1.10 |
|     | 30  | 1 | 1.46 | 1.92 | 1.72 |
| D   | 30  | 1 | 1.04 | 1.54 | 2.14 |
|     | 60  | 1 | 1.28 | 3.13 | 4.15 |
| E   | 40  | 1 | 1.90 | 4.25 | 4.80 |
|     | 60  | 1 | 1.76 | 3.79 | 6.98 |
| F   | 20  | 1 | 1.59 | 2.35 | 3.14 |
|     | 40  | 1 | 0.93 | 1.02 | 1.72 |

In certain cases (as in the preceding section) the tensile strength is higher than the original after short aging periods.   The effect is not nearly so noticeable here, but aging rates $R$ have, nevertheless, been calculated by comparing the time required to decrease the tensile strength by an arbitrary amount, usually 1000 pounds per square inch, over the smooth portion of the curve:

$$R = T_3/T_4$$

FIGURE 8
STOCK A
15 MINUTE CURE

FIGURE 9
STOCK A
30 MINUTE CURE

FIGURE 10
STOCK B
15 MINUTE CURE

FIGURE 11
STOCK B
30 MINUTE CURE

FIGURE 12
STOCK C
15 MINUTE CURE

FIGURE 13
STOCK C
30 MINUTE CURE

FIGURE 14    STOCK D    30 MINUTE CURE

FIGURE 15    STOCK D    60 MINUTE CURE

FIGURE 16    STOCK E    40 MINUTE CURVE

FIGURE 17  STOCK E
60 MINUTE CURE



FIGURE 18  STOCK F
20 MINUTE CURE

☐ 0.5 P.S.I.
△ 50 P.S.I.
○ 150 P.S.I.
X 300 P.S.I.

DAYS AGING



FIGURE 19  STOCK F
40 MINUTE CURE

DAYS AGING

where $T_3$ = time required for tensile strength to decrease by the chosen amount at 0.5 lb.

$T_4$ = corresponding time for higher pressures

Table VI tabulates the values of $R$.

### TABLE VI
#### EFFECT OF DROP IN TENSILE STRENGTH ON RELATIVE AGING RATE

| Stock | Time of cure (min.) | Drop in tensile (lb./sq. in.) | $R$ at gauge pressure of: | | | |
|---|---|---|---|---|---|---|
| | | | 0.5 | 50 | 150 | 300 |
| A | 15 | 4700–3700 | 1 | 1.31 | 1.67 | 1.96 |
| | 30 | 3600–2600 | 1 | 1.29 | 2.05 | 2.37 |
| B | 15 | 3400–2400 | 1 | 1.48 | 1.90 | 2.57 |
| | 30 | 2900–1900 | 1 | 1.05 | 2.52 | 2.74 |
| C | 15 | 2800–1800 | 1 | 0.89 | 1.25 | 1.09 |
| | 30 | 2800–1800 | 1 | 1.37 | 1.65 | 1.50 |
| D | 30 | 3000–2000 | 1 | 1.03 | 1.28 | 1.80 |
| | 60 | 3000–2000 | 1 | 1.29 | 3.19 | 4.55 |
| E | 40 | 2800–2000 | 1 | 1.85 | 4.06 | 4.87 |
| | 60 | 2800–2000 | 1 | 1.65 | 3.57 | 6.74 |
| F | 20 | 2900–2100 | 1 | 1.76 | 2.23 | 3.83 |
| | 40 | 2600–1600 | 1 | 0.87 | 1.22 | 1.85 |

The fact mentioned above, *i.e.*, that the rate of aging increases with increase in pressure but is not proportional to it, is clearly brought out by the values in Table VI. Thus, for stock A, a 20.7-fold increase in oxygen pressure causes less than a 2-fold increase in rate, or, for wire stock D, a 4.25-fold increase in pressure results in almost no increase in rate. Low-sulfur stock C appears to be only slightly affected by changes in pressure, but the reliability of these results may be questionable because of the peculiar trend of the values of $R$.

There is a great difference between stocks in their reaction to changes in pressure. For the short cures, changes in pressure from 0.5 to 300 pounds per square inch result in rate changes varying between 1.09 and 4.87, which is a difference of almost 350 per cent from the lowest to the highest value. The practical effects of these large differences in rate are the same as those described in the preceding section, so it is obvious that changes in the pressure of the oxygen pressure test should not be made unless each set of specifications is converted to the new pressure by individual study.

As was observed during the study of changes in temperatures, changes in pressure have a pronounced effect on the rate of aging of different cures of the same stock. Table VII shows the percentage change in the values of $R'$ and $R$

### TABLE VII
#### CHANGE IN RELATIVE RATES OF AGING BETWEEN TWO STATES OF CURE

| Stock | % Difference in $R'$ at: | | | % Difference in $R$ at: | | |
|---|---|---|---|---|---|---|
| | 50 lb. | 150 lb. | 300 lb. | 50 lb. | 150 lb. | 300 lb. |
| A | 1.5 | 13.5 | 21.0 | 1.5 | 23.0 | 21.0 |
| B | −23.5 | 29.0 | −2.0 | −29.0 | 32.5 | 6.5 |
| C | 72.0 | 46.5 | 55.5 | 54.0 | 32.0 | 37.5 |
| D | 23.0 | 103.0 | 111.0 | 25.0 | 149.0 | 153.0 |
| E | − 7.5 | −11.0 | 45.5 | −11.0 | −12.0 | 38.5 |
| F | −40.5 | −58.5 | −45.0 | −50.5 | −45.5 | −51.5 |

between the two states of cure studied. A negative change indicates that the rate of deterioration is slower at the higher state of cure.
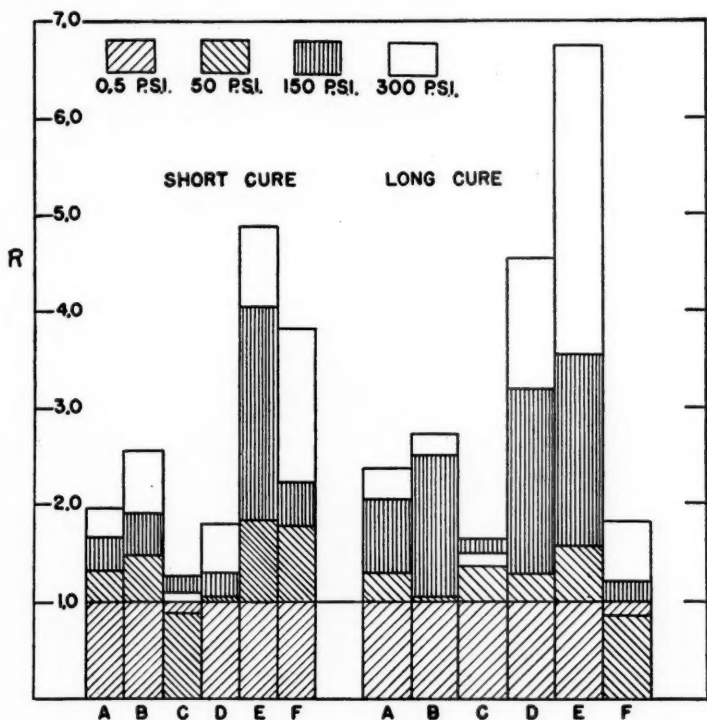


Fig. 20.—Summary of pressure effects.

It will be noticed that the state of cure has an appreciable effect on the rate of aging of every stock tested. Figure 20 is a graphic summary of these pressure effects. The large differences between stocks are clearly brought out.

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